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THE THEORY AND PRACTICE OF ACID MIXING

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PREFATORY NOTE

This is the fourth of a special series of reports which are being published in order to make available for the benefit of the industries concerned, results of scientific and industrial value contained in the technical records of the Department of Explosives Supply of the Ministry of Munitions. The work recorded in these Reports was done at, or in connexion with, some of the National Factories during the war. The preparation of the necessary abstracts of information was begun by the Ministry of Munitions at the close of the war, and arrangements were afterwards made by the Department of Scientific and Industrial Research to complete them. The Department wish it to be clearly understood that the interesting information contained in this series of reports is the result of the labours of the Ministry of Munitions, and is being compiled by Mr. W. Macnab, C.B.E., F.I.C., an officer of that Ministry now attached to the Department. The first three reports in the series, "Recovery of Sulphuric and Nitric Acids from Acids used in the Manufacture of Explosives: Denitration and Absorption," "Manufacture of Trinitrotoluene (TNT)," and "Sulphuric Acid Concentration," have already been published for the Department by His Majesty's Stationery Office.

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INTRODUCTION.

In any factory engaged in the manufacture of nitrated products, the Acids Section, which is responsible for the preparation of the mixed acids used in the nitration processes, should be organised as far as possible on rational and standardised lines. The need for a carefully regulated acids cycle is emphasised in the case of operations in which it is necessary to carry large stocks of acid in process. Instances of this kind are afforded in explosives manufacture, where the quantity of acid used greatly exceeds the bulk of the nitrated product produced. Thus, in the production of nitrocellulose, only a comparatively small proportion of the nitric acid content of the fresh mixed acid is removed during the nitration stage, and, as will be seen later, the manipulation of the acid resulting from this stage furnishes an excellent example of acid balance on a large scale. Somewhat similar instances arise in the production of nitroglycerine and of TNT, and it is the purpose of this publication to indicate the methods adopted in drawing up the necessary acid balances for these manufactures.

Having arrived at a satisfactory scheme with regard to the theoretical side of the acid cycle, it is essential that the quantities stipulated in the acid balance should be realised as far as possible in practice. For the normal working of any acid factory there is an optimum position in respect of acid stocks which it is the aim of the acids manager to maintain. To attempt to control plant output by reference to the stocks alone is impossible however, since the quantity and variety of acid in stock can successfully conceal any tendency toward over or under production until these have become pronounced; in other words, the control would pass from the acids manager to the storage tanks. Moreover, a plant will be more economically operated if the output is steady and not fluctuating from day to day or from week to week, for it is obviously unsound, both from considerations of the plant and of the operatives, for the working to be of a spasmodic or intermittent nature. An account is given in Section I of the methods which have been devised in Government explosives factories in order to represent graphically the figures obtained from the daily stock sheets and other plant returns, so that the closeness with which the acids balance is being followed may be determined at a glance, and any deviations from schedule may be checked before they have assumed troublesome proportions.

Since the plant and process for acid mixing may be said to form the main controlling factor in the acid cycle as a whole, a detailed description of these is given, reference being made at the same time to the calculations involved in mixing acids of varying strengths to obtain sulpho-nitric acids of constant composition. This description takes the form of an account of the TNT acid mixing plant at H.M. factory, Queen's Ferry, which completes the account of the TNT process at that factory, the nitration section having already been described.*

The following abbreviations are used throughout, viz., TNT for trinitrotoluene, MNT for mononitrotoluene, NG for nitroglycerine, GC for guncotton, and NC for nitrocellulose.

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* "Manufacture of TNT and its intermediate products," No. 2 of this Series.

SECTION

ACID CYCLES, ACID BALANCES, AND CONTROL OF PLANT OUTPUT.

General.—In the following account it is proposed to describe in detail the methods used in drawing up acid balances to control the cycle of acid production and recovery in the manufacture of trinitrotoluene, nitroglycerine, and nitrocellulose. Although the methods adopted in these three cases are intrinsically the same, yet the widely varying processes used in the production of these three explosives render a certain amount of divergence in procedure essential. This is not the case, however, as regards the plants necessary for producing and recovering the acids used, and the TNT acid mixing plant described in Section 3 may be taken as a standard type for the three processes.

TNT ACID CYCLE.

Acid Plants.—In any self-contained factory manufacturing TNT, the following acid units are required :—

(1) Plant for producing oleum.
(2) Plant for concentrating sulphuric acid.
(3) Plant for denitrating the spent acids resulting from the nitration stages.
(4) Plant for absorbing and returning to process in the form of weak nitric acid the degradation products of nitric acid resulting from (3).
(5) Plant for the production of strong nitric acid.
(6) Plant for washing nitre bags to recover the residual nitre therefrom.
(7) Acid mixing plant.
(8) Storage capacity for sulphuric, nitric, fresh mixed, and spent acids, &c.

It is not the intention here to refer in detail to these plants, other than that for acid mixing, but a brief summary of the function of each as applied to TNT manufacture will now be given.

Mixed Acids.

Two mixed acids are produced at the acid-mixing plant, viz. :—

(*a*) TNT mixed acid of composition :—

	Per cent.
H_2SO_4	79·5
HNO_3	17·8
H_2O	2·7
	100·0

and (*b*) MNT mixed acid of composition:—

	Per cent.
H_2SO_4	62·0
HNO_3	21·0 [*]
H_2O	17·0
	100·0

For reasons which need not be discussed here, it was decided not to use at Queen's Ferry the nitration scheme in which the waste acid from the trinitration stage is revivified with nitric acid and utilised for the mononitration stage. Both TNT and MNT nitration acids, therefore, are mixed entirely from fresh acids, *i.e.*, all spent acid is denitrated, and no portion of it is revivified or otherwise utilised in the preparation of further quantities of mixed acid.

Spent Acids.

The spent acids produced are as follows:-

(*a*) TNT spent acid of composition:—

	Per cent.
H_2SO_4	71·2
HNO_2	3·3
H_2O	25·5
	100·0

The difference in dilution between the mixed and spent acids represents water formed during nitration, together with water added during the nitration stages to secure separation of the nitrotoluenes in solution. The spent acid usually contains approximately 1 per cent. of nitro-compounds (consisting chiefly of mono- and dinitrotoluene) when received at the denitration plant. The proportion of water added during the nitration stages is calculated to give a content of 71 per cent. of H_2SO_4 in the spent acid, so as to bring the latter as near as possible to the 70 per cent. strength necessary for denitration.

(*b*) MNT spent acid of composition:—

	Per cent.
H_2SO_4	72·3
HNO_2	0·5
H_2O	27·2
	100·0

The nitro body is present in this acid to the extent of about 0·5 per cent. The increase in dilution from mixed acid to spent acid is due in this case wholly to the formation of water during nitration, no water being added directly. The composition of the mixed acid is calculated to give an H_2SO_4 content of 72·5 per cent. in the spent acid. This figure is higher than the 71 per cent. for TNT spent acid, but 72·5 per cent. sulphuric acid is regarded as the minimum safe strength for storing in the steel tanks at the MNT plant, and for delivering through wrought-iron pipe-lines to the Acid Section.

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[*] The HNO_3 figure shown in the diagram, Fig. 1, includes the HNO_2 content, and is 0·2 per cent. higher than is given above.

Denitration and Absorption Plants.

No difference is made at the denitration plant as regards the treatment of the two varieties of spent acid. A mixture of the two acids is charged to the denitrating column, and, so far as the denitrators, concentrators, retorts, and oleum plant are concerned, the acids are treated as though a single acids cycle were in operation.

The difference in dilution of the spent acid and resulting denitrated acid represents the steam absorbed during the denitration stage, and the system recently introduced of preheating the acid before denitration has aimed at reducing this increase to the lowest possible limits.

The nitrous gases liberated during nitration, after passing through a series of absorption towers, are finally recovered in the form of weak nitric acid (50 to 51 per cent. HNO_3) which is utilised for mixing purposes.

Concentration Plant.

The customary method of procedure in the Queen's Ferry acids cycle utilises the oleum plant, as well as the ordinary concentrators, for concentrating the weak sulphuric acid. The sulphur trioxide produced at the Grillo oleum plant is absorbed directly in the concentrated acid from the Gaillard concentration plant.* The Gaillard towers have, therefore, to remove the water entering the cycle at the MNT and TNT nitration plants and at the denitrators, less the amount of water in the sulphuric acid charged as feed acid to the nitric acid retorts, and the amount lost in acid spilled or otherwise consumed or lost in the cycle.

Oleum Plant.

This plant is worked to produce two varieties of acid, viz.,

(*a*) 20 per cent. oleum,
and (*b*) 98·6 per cent. sulphuric acid.

All the concentrated acid produced at the concentrators is delivered to the oleum plant, with the exception of a small amount used in the preparation of MNT mixed acid, and a larger quantity used, together with Grillo 98·6 per cent. sulphuric acid, for the mixing of feed acid for the nitric acid retorts.

In general, two Grillo units produce oleum, whilst the remaining four are operated to yield 98·6 per cent. sulphuric acid. This procedure provides a surplus of oleum, which is easily worked off at the acid mixing plant whenever it shows any tendency to accumulate. The sulphur trioxide entering the cycle at the Grillo plant balances the total losses of SO_3 in the cycle, including the SO_3 content of the retort feed acid.

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* Weak sulphuric acid *ex* Grillo plant being concentrated at the NC Acids Section, it follows that only SO_3 enters the TNT acids cycle from the Grillo plant.

Nitric Acid Plant.

A small mixing plant adjacent to the nitric acid retort houses supplies a uniform 93 per cent. feed acid, the H_2SO_4 usage at the retorts being approximately

$$\frac{H_2SO_4}{NaNO_3} = 0{\cdot}9.$$

No "cut" is made in the nitric acid produced, *i.e.*, the whole of the acid recovered, including both weak and strong acids, is run into lead receivers, yielding an acid of 87 per cent. average strength. The only weak nitric acid collected separately comes from the absorption towers.

Mixing Plant.

The whole of the weak nitric acid produced by the absorption towers at the denitration and nitric acid plants is utilised for MNT mixed acid, the balance of nitric acid for this acid being made up of strong acid from the retorts. Sulphuric acid of approximately 95 per cent. strength is required in order to yield a mixture of the desired composition. This is secured by making two standard mixes, one with Grillo 98·6 per cent. sulphuric acid, which affords a ready and rapid means of mixing off the weak nitric acid as it is produced, and the other with concentrated acid from the Gaillard towers, which introduces the strong nitric acid from the retorts necessary to make up the required quantity of MNT mixed acid.

TNT mixed acid is always mixed from oleum, 98·6 per cent. sulphuric acid, and strong nitric acid. No weak nitric acid is, as a rule, introduced into the mixed acid.

Contrast between Flow Sheet and Acids Balance.—The usual preliminary to the understanding or control of an acids cycle is the calculation of what has been called the "Acids Balance." It is necessary to distinguish this clearly from the flow sheets,[*] examples of which are given on pages 6A and 6B, which are issued monthly by the Statistical Section. The acids balance is in itself, of course, a flow sheet, but there are several essential differences between the two which need to be recognised:—

(*a*) The flow sheet merely summarises the records of the actual working of the various plants over a particular period, and it by no means follows that they will be operated in accurate "balance" during any period of working. According to the relative efficiencies of the various plants, the stocks of acids and the total tonnages of SO_3 and HNO_3

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[*] A detailed description of the technical records and other plant returns from which these flow sheets are drawn up is given in the "Report on the Statistical Work of the Factories Branch," published by H.M. Stationery Office.

in circulation will fluctuate from month to month. The acids balance attempts to forecast conditions of working, which will keep the acids in the cycle in accurate balance and at the same time maintain a fixed, pre-determined total of SO_3 and HNO_3 in circulation.

(*b*) The efficiencies of plants vary from month to month, particularly when they are hard pressed to produce their maximum output. These variations affect different plants for different months, so that the workings of successive months are seldom comparable. No single month can be regarded as representing average working conditions.

(*c*) In addition to these more or less accidental variations, improvements in modes of working take place continually, which render the records of past working unsuitable, unless modified, as a programme for future working.

Only in the case of a process which has become standardised and stereotyped in its methods of working would, for example, 12 months average working, as represented by a yearly flow sheet, constitute a satisfactory basis for future control. In the case of a process which is developing, the main value of the six or twelve months flow sheet is to indicate the progress which has been made since the period in question.

The Acids Balance.—In order to be satisfactory, an acids balance should show:—

(*a*) The flow sheet quantities for average working efficiencies, indicating clearly what these efficiencies are. The quantities given must, of course, be such as will preserve an accurate balance of acids in the cycle.

(*b*) The variations to be made in the "average" quantities on account of all possible variations in plant efficiencies and other abnormalities in the working of the cycle.

The considerations outlined above will serve to indicate the difficulty in making out what may be called the average acids balance. Short-period flows sheets are unsatisfactory, on account of the errors introduced by such factors as faulty measurement, *i.e.*, errors which more or less level up when figures are taken over a longer period. The average acids balance given in Fig. 1 was derived mainly from the half-yearly flow sheets for the periods July—December, 1917, pages 6A and 6B. During this period efficiencies and methods of working were fairly steady, and the figures given can be regarded as fair averages of normal working.

Checks to the working of the Acids Cycle.—In order to be quite certain of the satisfactory working of the cycle, it is advisable, in addition to constructing the acids balance, to devise suitable and easily applied methods of checking the results of its application. The points referred to in this and the preceding paragraph will now be taken in order.

Calculation of the Average Acids Balance.

This will be given in some detail, in order to make quite clear the method employed.

Nitration Quantities.—The two main sets of figures taken from the flow sheets are those for mixed acids supplied to the MNT and TNT nitration plants and for the spent acids received from them. All figures dealt with are for 100 tons of TNT.

Acid.	—	H_2SO_4.	H_2SO_4.	HNO_3.	HNO_3.
	Tons.	Percent.	Tons.	Percent.	Tons.
TNT mixed acid	485·6	79·5	386·1	18·0	87·4
TNT spent acid	516·3	71·2	367·6	4·43	22·9
Consumption at trinitration stage	—	—	18·5	—	64·5
MNT mixed acid	162·0	62·0	100·4	21·2	34·3
MNT spent acid	132·7	72·3	95·9	0·7	0·9
Consumption at mononitration stage	—	—	4·6	--	33·4

The percentage of HNO_3 in the mixed acids in the above tables includes 0·2 per cent. of HNO_2 calculated as HNO_3.

The nitrous acid in the spent acids is also expressed as HNO_3. On the basis of these figures, the acids balance will next be calculated for the various plants in order.

Denitration Plant.—The data for this plant require to be worked out first of all, in order to ascertain the tonnage of HNO_3 recovered. The output from the retorts is directly dependent upon this figure, inasmuch as they have to supply the difference between the total HNO_3 content of the mixed acid and that recovered from the denitrators.

(a) *Received by Denitrators.*

	H_2SO_4.	HNO_3.
	Tons.	Tons.
TNT spent acid	367·6	22·9
MNT spent acid	95·9	0·9
Total	463·5	23·8

No part of these acids is revivified, the whole being denitrated and concentrated.

(b) *Recovery of HNO_3.*

The flow sheet gives an average recovery of 80·63 per cent.; an even 80 per cent. will be assumed for purposes of calculation on this assumption—

Amount of HNO_3 recovered = 19·0 tons.
Amount of HNO_3 lost = 4·8 tons.
Average strength of nitric acid recovered = 51 per cent. HNO_3.
∴ Amount of nitric acid obtained from the denitrators = 37·3 tons.

(c) *Recovery of* H_2SO_4.

The flow sheet gives 0·58 per cent. loss. Taking 0·6 per cent. loss an even figure, then—

Loss on 463·5 tons H_2SO_4 = 2·8 tons.
∴ Amount H_2SO_4 recovered = 460·7 „

With the system of pre-heating spent acid before charging it to the denitration columns, the denitrated acid is produced at a strength of 68 per cent. H_2SO_4.

$$\therefore \text{Amount of denitrated acid} = \frac{460 \cdot 7}{0 \cdot 68} = 677 \cdot 5 \text{ tons.}$$

Nitric Acid Plant.—The HNO_3 requirements for 100 tons of TNT are as follows:—

For TNT mixed acid - - - - - - -	87·4 tons.
For MNT mixed acid - - - - - - -	34·3 „
Total - - - - - - - -	121·7 „
Less quantity recovered at denitrators - -	19·0 „
Difference - - - - - - - - -	102·7 „

This quantity must be supplied by the retorts, and at an average strength of 87·0 per cent., requires 118·0 tons of nitric acid. The average efficiency of the retorts over the six months was 94·6 per cent.; a fair standard figure for the present purpose is 95 per cent.

∴ Amount of HNO_3 (as $NaNO_3$) to be charged =

$$\frac{102 \cdot 7}{0 \cdot 95} \text{ - - - - - - - - - } = 108 \cdot 1 \text{ tons}$$

∴ Amount of $NaNO_3$ to be charged - = 145·8 „

Amount of dry sodium nitrate (98 per cent. $NaNO_3$) - - - - - - - - = 148·8 „

The calculation of the tonnage of feed acid for the retorts requires a further deviation from the flow sheet.

The ratio $\frac{H_2SO_4}{NaNO_3}$ for the half year was 0·993.

This was shortly afterwards reduced to 0·97, which will certainly be sustained. An attempt is being made to reduce it still further to 0·95, but it remains to be seen whether such a figure is feasible when a high output is demanded.

On the basis of a 0·97 ratio, therefore—

H_2SO_4 required for feed acid $= \frac{145 \cdot 8}{0 \cdot 97} = 141 \cdot 4$ tons.

Equivalent weight of 93 per cent. sulphuric acid - - - - - = 152·0 tons.

Assuming, as will be calculated later, that the Gaillard concentrated acid contains 90·4 per cent. H_2SO_4, the retort feed acid will consist of 48·2 tons of 98·6 per cent. sulphuric acid and 103·8 tons of 90·4 per cent. sulphuric acid.

Gaillard Tower Concentration Plant.—Amount of H_2SO_4 received from denitrators (*see* page 8) = 460·7 tons. The loss is given on the flow sheet as 2·49 per cent., but this includes losses prior to the operation of the Cottrell precipitation plant for recovery of the sulphuric acid in the exit gases from the Gaillard towers; 1·5 per cent. is a fair present figure.

∴ H_2SO_4 lost during concentration = 6·9 tons.

H_2SO_4 recovered - - - - = 453·8 „

The requisite degree of concentration obviously cannot be calculated until all the other details of the cycle have been worked out.

Mixing Plant.

(*A*) *TNT Mixed Acid.*

This is mixed from retort nitric acid and Grillo 98·6 per cent. acid and oleum.

Amount required (*see* page 7) = 485·6 tons (386·1 tons H_2SO_4; 87·4 tons HNO_3).

Tonnage of nitric acid at 87 per cent. HNO_3 required = 100·5 tons.

∴ Tonnage of sulphuric acid required = (485·6 − 100·5) = 385·1 tons.

Strength of sulphuric acid required $= \frac{386 \cdot 1 \times 100}{385 \cdot 1} = 100 \cdot 3$ per cent. H_2SO_4.

If x is the amount of oleum (105 per cent. H_2SO_4), and y the amount of 98·6 per cent. sulphuric acid required, then—

$$x + y = 385 \cdot 1$$

$$1 \cdot 05x + 0 \cdot 986y = 385 \cdot 1 \times 1 \cdot 003 = 386 \cdot 26$$

whence $x = \frac{6 \cdot 55}{0 \cdot 064} = 102 \cdot 3$ tons, and $y = \frac{18 \cdot 1}{0 \cdot 064} = 282 \cdot 8$ tons.

In order to obtain 485·6 tons of mixed acid from the acids available therefore, it is necessary to mix—

Nitric acid (87 per cent. HNO_3) - - - -	100·5 tons.
Oleum (105 per cent. H_2SO_4) - - - -	102·3 „
Sulphuric acid (98·6 per cent. H_2SO_4) - -	282·8 „
Total - - - - - -	485·6 „

(B) MNT Mixed Acid.

This utilises all the nitric acid *ex* denitrators, the remainder of the HNO_3 required coming from the retorts.

Amount required (*see* page 7) = 162·6 tons containing 100·4 tons of H_2SO_4 and 34·3 tons of HNO_3.

HNO_3 from denitrators = 19·0 tons = 37·3 tons of nitric acid containing 51 per cent. of HNO_3.
HNO_3 from retorts = 15·3 tons = 17·6 tons of nitric acid containing 87 per cent. of HNO_3.
Total = 34·3 tons HNO_3, or 54·9 tons of nitric acid.

∴ Tonnage of sulphuric acid required = (162 − 54·9) = 107·1 tons.

Strength of sulphuric acid = $\frac{100{\cdot}4 \times 100}{107{\cdot}1} = 93{\cdot}75$ per cent. H_2SO_4.

This is mixed from Gaillard sulphuric acid and Grillo 98·6 per cent. sulphuric acid. The quantities cannot be calculated until the Gaillard concentration has been worked out. This figure will be shown later to be 90·4 per cent. (page 11).

The necessary proportions in which these acids must be utilised are calculated in a similar manner to *TNT mixed acid* above, and will be found to be as follows:—

Sulphuric acid (98·6 per cent.) - - - -	43·8 tons.
Sulphuric acid (90·4 per cent.) - - - -	63·3 ,,

Grillo Oleum Plant.—This plant produces sulphur trioxide to make good all SO_3 losses in the cycle.

(a) H_2SO_4 Losses in Cycle per 100 tons of TNT.

	Tons.
At TNT nitration plant - - - - - -	18·5
At MNT nitration plant - - - - - -	4·6
At denitration plant - - - - - -	2·8
At concentration plant - - - - - -	6·9
Charged to retorts - - - - - -	141·4
Total - - - -	174·2

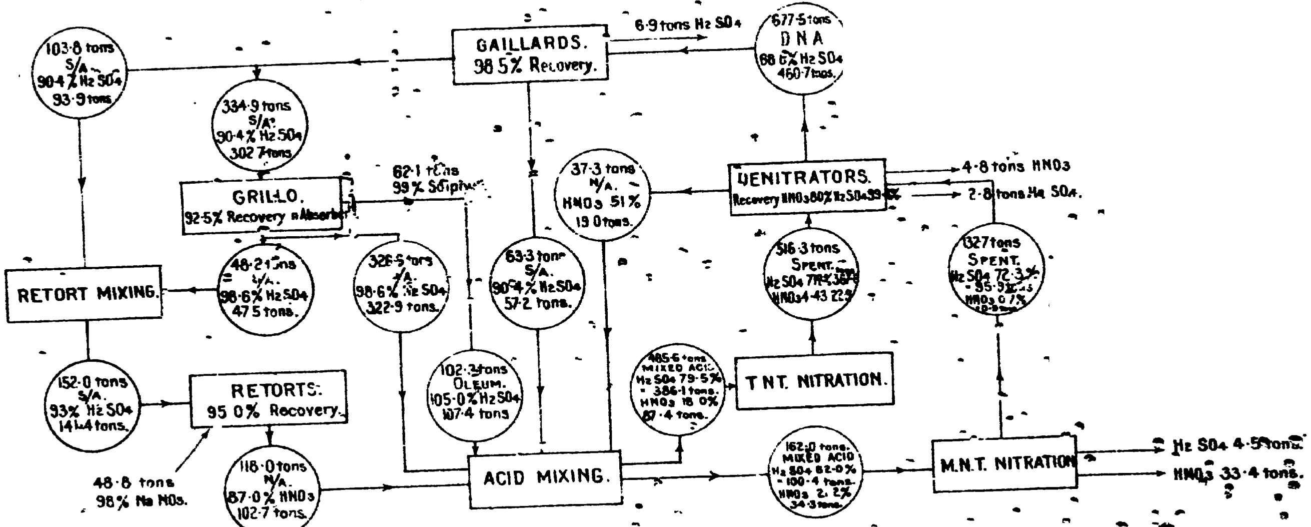
(b) *Corresponding SO_3 required from Grillo Plant.*

This quantity is $\frac{174{\cdot}2 \times 80}{98}$, *i.e.*, 142·2 tons, and to obtain the average balance, it will be assumed that the whole of this SO_3 is supplied as 98·6 per cent. acid and oleum. In practice, of the SO_3 charged to the Grillo plant, 92·5 per cent. is recovered in the absorption system and about 2·5 per cent. in the scrubbers. The

To Face p. 11.

H. M. FACTORY. QUEEN'S FERRY.

ACID BALANCE FOR 100 TONS TNT.


GAILLARDS. 98 5% Recovery.
6·9 tons H_2SO_4
677·5 tons D N A 68 6% H_2SO_4 460·7 tons.
103·8 tons S/A. 90·4% H_2SO_4 93·9 tons
334·9 tons S/A. 90·4% H_2SO_4 302 7 tons
GRILLO. 92·5% Recovery n Absorber
62·1 tons 99% Sulphur
37·3 tons N/A. HNO_3 51% 19 0 tons.
DENITRATORS. Recovery HNO_3 80% H_2SO_4 99%
4·8 tons HNO_3
2·8 tons H_2SO_4.
RETORT MIXING.
48·2 tons S/A. 98·6% H_2SO_4 47 5 tons.
326·5 tons S/A. 98·6% H_2SO_4 322·9 tons.
63·3 tons S/A. 90·4% H_2SO_4 57·2 tons.
516·3 tons Spent. H_2SO_4 71% HNO_3 4·43 22·9
327 tons Spent. H_2SO_4 72·3% = 35·9 HNO_3 0·7%
152·0 tons S/A. 93% H_2SO_4 141·4 tons.
RETORTS. 95 0% Recovery.
102·3 tons Oleum. 105·0% H_2SO_4 107·4 tons
485·6 tons Mixed Acid H_2SO_4 79·5% = 386·1 tons. HNO_3 18 0% 87·4 tons.
TNT. NITRATION.
48·8 tons 98% $NaNO_3$.
118·0 tons N/A. 87·0% HNO_3 102·7 tons.
ACID MIXING.
162·0 tons. Mixed Acid H_2SO_4 62·0% = 100·4 tons. HNO_3 2·2% 34·3 tons.
M.N.T. NITRATION
H_2SO_4 4·5 tons.
HNO_3 33·4 tons.

SUPPLEMENTARY NOTES.

	RAISE	LOWER
1. 100 tons TNT require 1 Grillo Unit on 68½ lbs. Sulphur Charges for 7 days.	%	%
2. Variation in Gaillard Concentration Figure.		
a. Increase of total H_2SO_4 losses at Nitration, Denitration and Concentration by 10 tons per 100 tons TNT.		0·4
b. Increase of total HNO_3 losses at Nitration by 5 tons per 100 tons TNT.		0·4
c. Lowering of Retort Efficiency by 1·0%		0·1
d. Increase of Denitrator-Efficiency by 5%	0·2	
e. Increase of $H_2SO_4/NaNO_3$ ratio on Retorts by 0·01 (from ·97.		0·1

	RAISE	LOWER
f. Increase in dilution of Retort N/A by 1·0%	0·3	
g. Increase in dilution of Denitrator N/A by 1·0%	0·14	
h. Decrease in TNT. Mixed Acid consumption by 10 tons per 100 tons TNT.		0·2
i. Decrease in M.N.T. Mixed Acid consumption by 10 tons per 100 tons TNT.		0·1
j. Import of 100 tons Oleum per week.	0·4	
k. Import of 100 tons 93% S/A per week.	0·7	
l. Import of 100 tons Scrubber Acid per week (63·0%)	0·5	
m. Use of 10 tons Spent Acid per week for Mixing	0·06	

Variations j–m are calculated on an output of 700 tons TNT per week.

FIG. 1

scrubber acid went formerly to the nitrocellulose cycle; a correction factor was introduced later, to show the effect of its introduction into the TNT acid cycle.

Acids Balance.—It is necessary to strike a balance in order to arrive at the degree of concentration which must be worked to at the Gaillards towers. This is possible, since the tonnage of concentrated acid plus tonnage of SO_3 added at the Grillo plant is equal to the tonnage of acids required for the mixing plant and the retorts.

This balance works out as follows :—

Gaillard Towers.	*Tons.*	*For Mixing.*	*Tons.*
H_2SO_4	453·8	(a) *TNT mixed acid* :—	
Water	x	Oleum (105 per cent. H_2SO_4)	102·3
		Sulphuric acid (98·6 per cent. H_2SO_4)	282·8
Grillo plant :—		(b) *MNT mixed acid* :—	
		Sulphuric acid (93·75 per cent. H_2SO_4)	107·1
		For retorts :—	
SO_3	142·2	Sulphuric acid (93·0 per cent. H_2SO_4)	152·0
Total	596·0 + x	Total	644·2

∴ Tonnage of water in Gaillard towers acid (644·2 — 596) = 48·2 tons.

∴ Percentage of H_2SO_4 in Gaillard towers acid $= \frac{453·8 \times 100}{453·8 + 48·2}$ = 90·4 per cent., and the amount required is 453·8 + 48·2 = 502 tons.

Acids Balance Diagram.—The accompanying diagrammatic acids balance (Fig. 1) has been constructed from the foregoing figures. The working out of this balance presents no difficulty except in regard to the acid supplied to the Grillo oleum plant. This is the residue of the Gaillard concentrated acid, after supplying the amount of acid calculated as necessary for the retort mixing and TNT mixing plants.

In this average acids balance only the recovery in the Grillo absorption towers (92·5 per cent.) is reckoned in calculating the amount of sulphur to be burned at the Grillo plant.

SO_3 required - - - - - - - 142·2 tons.
Corresponding weight of sulphur - - - 56·9 „

∴ Weight of sulphur to be charged (based on a 92·5 per cent. efficiency, and sulphur containing 99 per cent. of sulphur) = 62·1 tons.

VARIATIONS IN THE WORKING OF THE ACIDS CYCLE.*

Having arrived at an average acids balance, it is necessary to consider the effect of variations in plant working and efficiencies upon the figures obtained.

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* The facts arrived at under this heading are summarised on the acid balance reproduced in Fig 1.

Points needing Control.—The three important points to be controll in the cycle are :—

(a) The concentration figure at the Gaillard towers.
(b) The rate of production of HNO_3 at the retorts.
(c) The production of SO_3 at the Grillo plant.

Of these, the first is the most important, since its effects are n immediately obvious, whereas the over-or under-production of HN or SO_3 is soon indicated by the position of the stocks of mixed unmixed acids. Provided the degree of concentration at the Gailla towers is satisfactory, the other factors in the cycle are easi controlled.

Factors necessitating variation in concentration.—The chief factors whi influence the degree of concentration at the Gaillard towers may classified as follows :—

(a) Total SO_3 losses in the cycle.
(b) Average strength of nitric acid used for mixing.
(c) Import of SO_3 into the cycle as sulphuric acid or as oleum.
(d) Use of spent acid for mixing.
(e) Variation in consumption of mixed acid.
(f) Export of SO_3 from the cycle.

The effect of these factors will be considered one at a time, assumi all other factors to remain at the figures given in the average aci balance. It will then be sufficiently accurate, for practical purposes, assume that the effect of any number of variations will be equal to t sum of the separate effects due to the variations considered singly. A calculations will be based on the figures for an output of 100 tons TNT.

Variation in SO_3 losses.—Considering SO_3 as H_2SO_4, these losses m be divided into two classes, viz. :—

(a) Losses during nitration, denitration, and concentration, 32 tons H_2SO_4.
(b) Charged to nitric acid retorts, 141·4 tons H_2SO_4.

The effect of these on the acids balance will now be discussed.

(a) *Increase of H_2SO_4 losses.*

Increase of H_2SO_4 losses by 10 tons of H_2SO_4 will decrease t amount of H_2SO_4 from the Gaillards by 10 tons, which corresponds an increased amount of SO_3 required from Grillo plant of 8·0 tons. T additional water to be left in the Gaillard sulphuric acid is therefo 2 tons, and on 502 tons this means a lowering of the concentrati figure by 0·4 per cent.

(b) *Increase of H_2SO_4 charged to the Retorts.*

Increase of H_2SO_4 charged to the retorts by 10 tons increases t SO_3 required from the Grillo plant by 8·0 tons, and the 93 per cen sulphuric acid required for the retorts by $\frac{10}{0{\cdot}93}$ tons, *i.e.*, 10·8 to

This increases the water (in the Gaillard concentrated acid) by 2·8 tons, and decreases the concentration figure by 0·56 per cent.

Consumption of H_2SO_4 at the Retorts.—This is affected in three ways, viz. :—

(a) By the efficiency of the Retorts.

Assuming a steady H_2SO_4 ratio, a lowering of the efficiency by 1 per cent. of $NaNO_3$ from 95 to 94 per cent. will increase the H_2SO_4 consumed by $\frac{141 \cdot 4}{95}$ tons, *i.e.*, 1·5 tons. As shown above, 10 tons increase in the consumption of H_2SO_4 lowers the Gaillard concentration figure by 0·56 per cent. An increase of 1·5 tons will therefore lower the concentration figure by 0·086 per cent. Hence, a lowering of 1 per cent. in the retort efficiency affects concentration by approximately 0·1 per cent.

(b) By the $\frac{H_2SO_4}{NaNO_3}$ *ratio.*

This was assumed to stand at 0·97; its increase by 0·01 will similarly increase the H_2SO_4 consumption and will decrease the concentration figure by 0·[illegible] per cent.

(c) By the total consumption of HNO_3 in the cycle.

This is the sum of the nitration and denitration losses, the average figure for which is 102·7 tons.

The reduction of this quantity by 5 tons would reduce the H_2SO_4 in the feed acid by 6·9 tons. Now, reduction by 10 tons raises concentration by 0·56 per cent. (*see above*), and reduction by 6·9 tons therefore raises concentration by approximately 0·4 per cent.

Effect of strength of Nitric Acid available.—Three points have to be considered here, viz. :—

(a) Variation in strength of Retort Nitric Acid.

Under average conditions, 118·0 tons of nitric acid are supplied by the retorts at 87 per cent, viz., 102·7 tons of HNO_3. If this is supplied at 86 per cent., the increased water content is 1·4 tons. The water content of the sulphuric acid used for mixing must be decreased correspondingly ; similarly the water content of the Gaillard acid.

The Gaillard concentration figure (on 502 tons of sulphuric acid) must therefore be raised 0·28 per cent.

(b) Variation in strength of Denitrator Nitric Acid.

With 80 per cent. recovery, the quantity of nitric acid recovered from the denitrators is 37·3 tons, which, at 51 per cent. is equivalent to 19·0 tons of HNO_3. Decrease in strength to 50 per cent. increases the water content by 0·7 tons, corresponding to a rise in concentration of 0·14 per cent.

(c) *Variation in denitrator efficiency.*

Since the amounts of HNO_3 produced by the denitrators and retorts are complementary, an increased recovery at the denitrators means an increase in the average dilution of the nitric acid available for mixing.

An increased denitrator efficiency of 5 per cent. means an increased recovery of 1·2 tons of HNO_3, *i.e.*, 2·4 tons of nitric acid at 51 per cent. This nitric acid replaces that which would have been supplied by the retorts at 87 per cent. The extra water introduced into the cycle is equal to the difference in the water content of the amounts of 51 and 87 per cent. nitric acid, each having an HNO_3 content of 1·2 tons. This figure is 1·0 ton, the effect being to raise the Gaillard concentration (on 502 tons) by 0·2 per cent.

Effect of import of SO_3 into the cycle.—The acids balance has been calculated on the assumption that all SO_3 losses will be made good by the supply of SO_3 free from dilution, by the Grillo oleum plant. When SO_3 enters the cycle in any other way, a certain amount of water is introduced along with it, and an equivalent amount of water must therefore be removed by the concentration plant. The production of SO_3 by the Grillo plant is, of course, reduced by an amount equal to the SO_3 content of the imported acid.

The following are the main cases to be considered. Calculations are based on a 700 ton weekly output of TNT; this means normally the production by the Gaillard towers of 3,500 tons of 90 per cent. acid.

(a) *Import of Oleum.*

This may be imported oleum from other factories, or surplus oleum from other parts of the same factory, which it is necessary for various reasons to work off in the TNT acid cycle.

If 100 tons of oleum are imported into the cycle in any week, this quantity at 105 per cent. H_2SO_4, contains 85·7 tons of SO_3 and 14·3 tons of H_2O. Hence the Gaillards will have to drive off 14·3 tons of extra water. On 3,500 tons, this will raise the concentration figure by 0·4 per cent.

(b) *Import of concentrated Sulphuric Acid.*

This may be surplus from other factories, or outstanding stock from the same factory. Taking this as containing an average of 93 per cent. H_2SO_4, 100 tons will contain 75·9 tons of SO_3 and 24·1 tons of H_2O. On 3,500 tons of Gaillard acid, this represents an increase in the concentration figure of 0·7 per cent. for every 100 tons of acid taken into the cycle in any single week. For ease in working, the increase in concentration can, of course, be spread over a number of weeks if so desired.

(c) *Import of scrubber Acid from Oleum Plant.*

The scrubber acid brought into the TNT acids cycle from the drying towers at the Grillo oleum plant is best regarded as an import, rather than attempting to reduce it to the routine of the average acids balance, particularly as the amount to be treated at the Gaillards will vary from week to week with the humidity of the atmosphere, and also with the amount of scrubber acid issued to other parts of the factory for various purposes.

Approximately 200 tons will require to be concentrated per week. The SO_3 content will include the 2·5 per cent. recovery in the scrubbing system of the SO_3 charged to the sulphur burners, and also the SO_3 content of the oleum fed to the strong acid scrubbing towers.

In regard to this scrubber acid, the Gaillard towers must certainly drive off a quantity of water equivalent to the whole of its water content. A portion of this is driven off, however, in concentrating it to the normal figure of 90·4 per cent. The concentration figure must be raised on the whole tonnage of acid dealt with, therefore, in order to drive off an amount of water equivalent to the water remaining in the scrubber acid after its concentration to 90·4 per cent. :—

200 tons of scrubber acid at 63 per cent. H_2SO_4 = 126·0 tons H_2SO_4.

200 tons of scrubber acid at 63 per cent. H_2SO_4 = 102·9 tons SO_3.

Corresponding tonnage of 90·4 per cent. sulphuric acid = 139·4 tons.

Water driven off in normal concentration to 90·4 per cent. = 200 — 139·4 = 60·6 tons.

Surplus water to be driven off = 139·4 — 102·9 = 36·5 tons.

139·4 tons of 90·4 per cent. sulphuric acid contain 100·8 tons of SO_3 and 38·6 tons of H_2O.

Total tonnage of 90·4 per cent. sulphuric acid per week = 3,500 + 139·4 = 3,640 tons (approximately).

∴ Necessary increase in concentration figure = 1·0 per cent.

The effect of introducing SO_3 into the system in any other form can be calculated in a similar way, care being taken to distinguish between SO_3 introduced directly into circulation as mixed acid or as retort feed acid, and SO_3 introduced as spent or other acid requiring concentration.

Use of spent Acid for mixing.—Whereas at Queen's Ferry no spent acid is revivified directly, a small amount of TNT spent acid is conveniently used from time to time to correct the dilution of MNT mixed acid. The use of 10 tons in a single week would have the following effect:—

10 tons of spent acid at 71 per cent. H_2SO_4 would be introduced into mixed acid. Ordinarily this would have come into circulation as concentrated acid at 90·4 per cent.

10 tons of spent acid at 71 per cent. H_2SO_4 contain 7·1 tons of H_2SO_4 and 2·9 tons of H_2O.

7·9 tons of concentrated sulphuric acid at 90·4 per cent. H_2SO_4 contain 7·1 tons of H_2SO_4 and 0·8 tons H_2O.

Extra water brought into circulation is therefore (2·9 — 0·8) viz., 2·1 tons.

On 3,500 tons of concentrated acid the degree of concentration must therefore be raised by 0·06 per cent.

The use of this small amount of spent acid does not, therefore, seriously interfere with the load on the concentrating plant.

Variation in the consumption of mixed Acid.—This is a fairly complex problem, and all that can be done here is to treat it approximately, which suffices for practical purposes. The main factor in the case of each mixed acid is its H_2SO_4 content and the tonnage of sulphuric acid used for mixing.

(a) *TNT mixed Acid.*

The total quantity normally required is 485·6 tons (see page 7). 385·1 tons of sulphuric acid, having an H_2SO_4 content of 386·1 tons, are used for mixing. Considering the effect of reduction in consumption by 10 tons, assuming the HNO_3 consumption to remain the same (variation in this factor having been treated separately), then, 10 tons of mixed acid require 8·0 tons of sulphuric acid containing 8·0 tons of H_2SO_4. The effect on the acids balance is to reduce the H_2SO_4 from the Gaillard towers by 8·0 tons (assuming the H_2SO_4 losses in the cycle to be constant), and to reduce the acid from the Grillo oleum plant by 8·0 tons.

Concentration figure $= \dfrac{(453{\cdot}8 - 8{\cdot}0)}{(502{\cdot}0 - 8{\cdot}0)} \times 100 = 90{\cdot}2$ per cent., *i.e.*, a lowering of 0·2 per cent.

(b) *MNT mixed Acid.*

The total quantity normally required is 162 tons, in the mixing of which 107·1 tons of sulphuric acid are used, having an H_2SO_4 content of 100·4 tons. Again considering the effect of reduction in consumption by 10 tons (an outside figure), 10 tons of mixed acid require 6·6 tons of sulphuric acid, containing 6·2 tons of H_2SO_4. The effect on the acids balance is to reduce the H_2SO_4 from the Gaillards by 6·2 tons, and to reduce the sulphuric acid from the Grillo plant by 6·6 tons.

The concentration figure therefore becomes—

$$\frac{(453{\cdot}8 - 6{\cdot}2)}{(502{\cdot}0 - 6{\cdot}6)} \times 100 = 90{\cdot}3 \text{ per cent., } i.e.,$$

a lowering in the degree of concentration of 0·1 per cent.

Export of Acid from the cycle.—This has the reverse effect to that of importing outside acid. Export is usually in the form of oleum, so that, using the argument put forward on page 14, the export of 100 tons in any week will require the concentration to be lowered by 0·4 per cent.

Control of the production of HNO_3 and SO_3.—It is not proposed to treat these in detail here. The actual amounts of each which are used per ton of TNT are obtained from the monthly flow sheets, and variations are at once apparent and easily adjusted, provided the rate of production of TNT is known.

The SO_3 required from the Grillo plant in any particular week is, of course, equal to the total SO_3 consumption in the production of the TNT to be manufactured, plus any SO_3 to be exported or required for any other purpose, and minus any SO_3 coming into the system in other form.

In regard to the Grillo plant also, it is customary to produce oleum in excess of the amount calculated as required for mixing. The surplus is mixed off with sulphuric acid from the Gaillards at the mixing plant. This does not affect the balance of the cycle.

CHECKS TO THE WORKING OF THE CYCLE.

Necessity for checks.—Checks are absolutely necessary to ensure that a cycle is working normally. In the absence of checks there is always the danger of stocks of acid getting out of balance, and, in particular, the accumulation or depletion of the amounts of acid in circulation. The greatest danger is the filling up of the available storage room with weak acid, which results either from too low a concentration figure, or from the inability of the concentration plant to concentrate to a sufficiently high figure the full amount of acid delivered to it. It is necessary to be able to detect this tendency before it reaches a serious stage. The checks which experience shows to be desirable are as follows:—

(*a*) Check of general balance of stock.

(*b*) Check of correct proportioning of production of TNT and MNT mixed acids at the acid mixing plant.

(*c*) Check of total acids in circulation.

Check of General Balance of Stocks.—It is obviously impossible in practice to preserve perfectly steady stocks, although their relative steadiness is a measure of the efficiency of the working of the cycle as a whole. It is necessary at times to close down individual plants for overhaul, burning out of flues, &c., and the stocks must permit of this being done. In general, the stocks of each acid should be such as to provide for each plant:—

(*a*) An ample margin of acid for working, in case the supply is cut off through a temporary closing down of the plant supplying the feed acid; and

(*b*) Sufficient empty storage to enable the plant to continue working when the plant normally taking its output is temporarily unable to do so.

The following table gives the acids in use on the TNT acids section, with the total storage accommodation, the tonnage of acid regarded as desirable, the spare storage thereby afforded, and the tonnage of acid treated per day on the basis of a 700 weekly output of TNT.

Acid.	Total Storage.	Desirable Stock.	Empty Storage.	Quantity treated daily.
	Tons.	Tons.	Tons.	Tons.
TNT spent acid - - - -	1,600	800	800	516·3
MNT spent acid - - - -	600	200	400	132·7
Denitrated acid - - - -	1,500	800	800	677·5
Concentrated acid - - - -	1,500	900	600	502·0
Retort feed acid - - - -	350	200	150	152·0
Grillo 98·6 per cent sulphuric acid -	1,000	500	500	382·5
Grillo oleum - - - -	550	200	350	102·9
Retort strong nitric acid - - -	60	30	30	125·1
Retort weak nitric acid - -	14	Nil	50	3·0
Denitrator nitric acid - -	8	4	4	37·3
TNT mixed acid - - - -	2,200	1,400	800	485·6
MNT mixed acid - - - -	700	200	500	162·0

It is worth while noting that whereas, in order to ensure continuous working the TNT nitrating houses need to carry a safe stock of mixed acid, the same consideration does not apply at the MNT section, where a considerable stock of MNT is always kept in hand.

The general balance can be readily checked when an agreement, such as is given above has been arrived at as to what constitutes a desirable condition of the stocks.

Check of relative outputs of TNT and MNT mixed Acids.—These quantities must be checked on account of the tendency for variation in the relative consumptions of mixed acid in the two nitration processes. The output of TNT mixed acid is checked satisfactorily by the condition of the total stock of TNT mixed acid. To check the production of MNT mixed acid the stocks of both MNT itself and MNT mixed acid must be taken into account. Assuming that a stock of MNT must be sustained as a stand-by in case of emergency, the most satisfactory procedure is to reduce any fluctuation in this to a corresponding tonnage of MNT mixed acid and then to check the steadiness of the figure so obtained.

Check of total Acids in circulation.—This cannot be satisfactorily done by merely totalling up the total acids in storage in the cycle. For example, the Grillo plant may over-produce SO_3 for a time, and stocks of Grillo sulphuric acid and oleum may accumulate. This does not affect the SO_3 in circulation, however, and in order to devise a check which will examine closely the satisfactoriness or otherwise of the Gaillard concentration during any period, it is necessary to define "circulation" in such a way as to obtain a figure which should remain constant with satisfactory working of the plants. This constant figure should include SO_3 in spent, denitrated, and concentrated acids, since these are obviously in circulation. As regards mixed acids, Grillo acids and retort feed acid, it is best to distinguish between the SO_3 content, which is true circulation acid, *i.e.*, SO_3 which comes from Gaillard concentrated acid, and the SO_3 component supplied by the Grillo, which is most satisfactorily regarded as out of circulation until it enters the spent acid tanks. Hence the SO_3 to be considered is reduced to the SO_3 in spent, denitrated, and concentrated acids, remembering that a portion of the latter acid is to be found in Grillo, mixed, and retort feed acids.

The necessary data are as follows:—

(a) *TNT spent Acid.*

100 tons at 71·2 per cent. H_2SO_4 contain 58·1 tons of SO_3.

(b) *MNT spent Acid.*

100 tons at 72·3 per cent. H_2SO_4 contain 59·0 tons of SO_3.

(c) *Denitrated Acid.*

100 tons at 68·0 per cent. H_2SO_4 contain 55·5 tons of SO_3.

(d) *Gaillard concentrated Acid.*

100 tons	at	90·0	per cent.	H_2SO_4	contain	73·5	tons of	SO_3.
100	,,	91·0	,,	,,	,,	74·3	,,	,,
100	,,	92·0	,,	,,	,,	75·1	,,	,,
100	,,	93·0	,,	,,	,,	75·9	,,	,,

(e) *Grillo Acids, Mixed Acids, and Retort feed Acids.*

The SO_3 in these acids which may be regarded as having come from Gaillard concentrated acid will vary with the concentration figure. The following table gives the tonnage for different concentration figures of SO_3 per 100 tons of each acid which may be reckoned as circulation acid:—

Acid.	Circulation SO_3 per 100 tons of acid when the concentration figure is—			
	90 per cent.	91 per cent.	92 per cent.	93 per cent.
	Tons.	Tons.	Tons.	Tons.
Grillo sulphuric acid (98·6 per cent.) -	54·1	56·3	58·8	61·3
Grillo oleum (105 per cent.) - -	39·7	41·4	43·1	45·0
Retort feed (93 per cent.) - - -	66·7	67·6	72·7	75·9
TNT mixed acid - - - -	39·9	41·5	43·4	45·3
MNT mixed acid - - - -	43·1	44·9	46·8	48·8

Given the foregoing figures, it is a matter of a few minutes to check the amount of SO_3 in circulation at any particular time. The result so obtained, although not correct to the nearest ton or so, is sufficiently accurate for ordinary purposes, and affords a ready and convenient method of testing the efficiency of the cycle.

CONTROL OF PLANT OUTPUT.

General.—As already outlined in the Introduction, for the normal working of any acid factory there is an optimum position with regard to stocks of acids which it is the aim of the person in charge of the Acids Section to maintain. To attempt to control the output of the plant by reference to the stocks alone, however, is impossible, since the quantity and variety of acid in stock is able to cover up any tendency towards over- or under-production until these have gone too far to allow of easy adjustment. In addition to the above considerations, it is essential for reasons of economy in labour and material that a steady output should be maintained. The following system was introduced in order that, as far as possible, a fixed programme might be drawn up for each individual plant which would correspond to the desired production of final product, and which would serve to maintain normal stocks of acids in process. Briefly, this method of control resolves itself into—

(*a*) The compilation of an *acids balance* to determine the work of each plant in terms of tons of final product (TNT, NC, NG, &c.).

(*b*) A system of *plant returns* which give the daily work and stocks of each plant.

(*c*) The *interpretation* of these returns by those in charge of the Acids Section.

Acids Balance.—This has already been described in the foregoing pages, and it is necessary at this point merely to summarise its functions, which are as follows:—the determination of the outputs required from each individual plant in terms of the final product, reference being made for this purpose to the results of former practice as summarised in the monthly quantity flow sheets (*see* pages 6*a* and 6*b*): the presentation of the information so obtained in the form of an acids balance or acid flow sheet (Figs. 1 and 2), which will show quite clearly the duty of each plant in terms of 100 tons of final product, so that, with a known weekly production of explosive, each plant can be given a definite programme to work to.

For example, the following programme for the week ending June 30th, 1917, which was based on a weekly production of 350 tons of TNT, is derived from the acids balance reproduced in Fig. 2:—

		Tons per diem.
TNT mixed acid required		256
MNT mixed acid required		78
Denitrators to treat	TNT spent acid	280
	MNT spent acid	62

Gaillard concentrators to concentrate 364 tons of denitrated acid to 92 per cent. strength (intentionally in excess of concentration figure shown, *vide infra*).

Nitric acid retorts to produce 52 tons of HNO_3.

Grillo oleum plant to produce 70 tons of SO_3 (intentionally below production figure shown, *vide infra*).

FIG. 2.—H.M. FACTORY—QUEEN'S FERRY.
Acid Balance for 100 *tons TNT.*

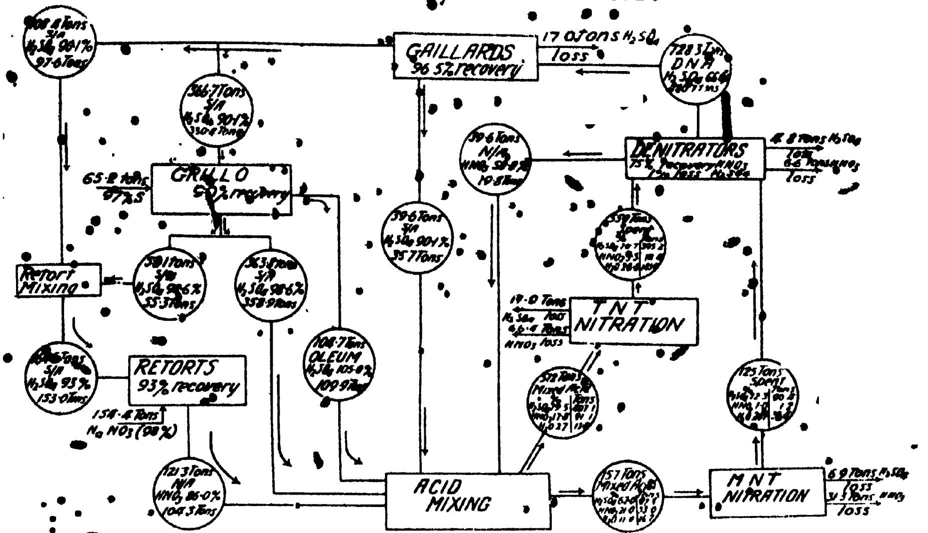

Table 1. **SUPPLEMENTARY NOTES.** **Table 2.**

98·6 Units. / 105 per cent Units.	Oleum made.	98·6 per cent. made.	90·1 per cent. feed to Grillo.	90·1 per cent to Mixers.	Remarks.
approx.	104·7	429·5	366·7	30·6	Flow sheet figures.
-	138·0	352·0	342·0	64·3	Most convenient for 350–450 tons TNT per week.
:2:3 -	172·5	301·5	316·0	90·3	
- -	207·0	241·2	290·2	116·1	
- -	258·7	150·8	251·5	154·3	
- -	276·0	120·6	238·6	167·7	
ll on 105 per cent.	345·0	—	187·0	219·3	For retort mixing, 32·1 tons oleum, and 132·4 tons, 90·1 per cent.

Tons TNT per Week	Sulphur charges using.					
	1 unit.	2 units	3 units.	4 units.	5 units.	6 units
525					89·5	70·3
500					80·4	67·0
475					76·4	63·6
450					72·4	60·3
425				85·9	68·4	56·9
400				80·4	64·3	53·6
375				75·3	60·3	50·2
350				70·3	56·3	46·8
325			87·1	65·3	52·3	43·5
300			80·4	60·3	48·3	40·2
275			73·7	55·2	44·2	36·8
250			[illegible]	50·2	40·2	33·[illegible]
200		80·4	53·6	40·2	32·2	26·8
100	80·4	40·2	26·8	20·1	16·1	13·4

Sulphur charges are based on 97 per cent., and a recovery of 90 per cent.

. TNT MIXED ACID.

H_2SO_4 HNO_3 H_2O

512 tons at 79·5, 17·8, 2·7 made from—

Tons.	Per cent.	Tons.	Tons.	Per cent.	Tons.
104·2 oleum,	105	H_2SO_4 = 109·2 H_2SO_4.	106·0 N/A	86·0	HNO_3 = 91·2 HNO_3.
301·3 S/A	98·6	„ = 297·1 „			

. MNT MIXED ACID.

H_2SO_4 HNO_3 H_2O.

157 tons at 62·0, 21·0, 17·0 made from—

Tons.	Per cent.	Tons.	Tons.	Per cent.	Tons.
62·5 S/A	98·6	H_2SO_4 = 61·6 H_2SO_4.	39·6 N/A	50·0	HNO_3 = 19·8 HNO_3.
39·6 „	90·1	„ = 35·7 „	15·3 „	86·0	„ = 13·2 „

. GRILLO PLANT.

Produces SO_3 to replace the following losses:—

At retorts - - - - -	153·0 tons H_2SO_4.	193·6 = 158·0 tons of SO_3.
At denitrators - - - -	4·8 „ „	
At Gaillards - - - -	17·0 „ „	
At TNT nitration plant - -	11·9 „ „	
At MNT „ „ - -	6·9 „ „	

The flow sheet gives a production of 419·9 tons of 98·6 per cent. acid and 104·7 tons of oleum. This s the minimum amount of oleum which may be produced; if more than this is made there will be a orresponding decrease in the amount of 98·6 per cent. acid, and the excess of oleum over 104·7 ton will e mixed with Gaillard acid (90·1 per cent.) at the mixing plant, producing again the flow sheet figure f 419·9 tons 98·6 per cent. acid. Table 1 shows the necessary changes in the acid circulation for varying quantities of oleum produced. This, in conjunction with Table 2, will show the number of Grillo units required working on oleum and on 98·6 per cent., and the necessary sulphur charge.

The quantities of mixed acids and spent acids (and therefore the consumption of H_2SO_4 and HNO_3 in TNT and MNT nitration), as well as the recoveries at the Gaillards and Grillo, are based on the 5 weeks practice—, 28th April to 2nd June, 1917. The recoveries at the denitrators and retorts, while higher than the actual figures for this period, are considered practicable.

Plant Returns.—In order to ascertain whether the various plants comprising the Acids Section are working to their programmes, *i.e.*, keeping in balance, and to indicate the acids position generally, two returns* are made each day, viz.:—

(1) The acids stocks at 6 a.m. (Fig. 3).

(2) The plant productions for the previous day (Fig. 4).

The stocks are given on the form illustrated in Fig. 3. Each column on the sheet represents the maximum storage capacity for one variety of acid, and the actual quantity of acid in stock at 6 am. is marked off as shown. The relation which the actual stock should bear to the storage capacity depends on various factors, and may vary from time to time. Taking the stocks as shown at 6 a.m. on the 26th June, for example, the only unsatisfactory stock is that of the TNT spent acid, which is greatly in excess of the normal, but adjustments in the acids balance had already been put into operation in order to reduce this stock.†

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* A complete set of the technical records prepared by H.M. factory, Queen's Ferry, for the month ending December 29th, 1917, are reproduced in the "Report on the Statistical Work of the Factories Branch," pp. 121–154. The forms on which the weekly records are made are practically identical with those used for monthly returns. The information given in the daily returns, from which Figs. 3 and 4 were compiled, are necessarily more detailed than that included in the weekly and monthly returns.

† Reduction of SO_3 stocks in spent acids and denitrated acid:—

(*a*) The excess and rate of reduction are fixed. If this rate is *c* tons per week, then, for a production of 350 tons of TNT per week this will become $\frac{c}{3{\cdot}5}$ per 100 tons of TNT.

(*b*) The SO_3 drawn from stock will mean a corresponding diminution in the amount required from the Grillo oleum plant of $(b - \frac{c}{3{\cdot}5})$.

(*c*) As before, the degree of concentration required at the Gaillard concentrators will be obtained from the balance of receipts and issues, viz.:—

From Gaillards—*x* tons of sulphuric acid. (= "*a*" tons of H_2SO_4)	To acid mixing—*q* tons of oleum (105 per cent.).
	To nitric acid retorts—*r* tons of sulphuric acid 93 per cent.
From Grillo—$b - \frac{c}{3{\cdot}5}$ tons of SO_3.	
	To export—*s* tons of sulphuric acid (*m* per cent.).
$x + b - \frac{c}{3{\cdot}5}$ tons.	$q + r + s$ tons.

e figure "*a*" above includes the SO_3 as H_2SO_4, drawn from stock, *i.e.*, $\frac{c}{0{\cdot}816 \times 3{\cdot}5}$)

∴ Degree of concentration required at Gaillard towers $= \dfrac{a \times 100}{q + r + s - b\left(\frac{c}{3{\cdot}5}\right)}$ per cent., and this figure must necessarily be greater than that shown on the acids balance in Fig. 2. (*See also* page 11.)

To face p. 22.

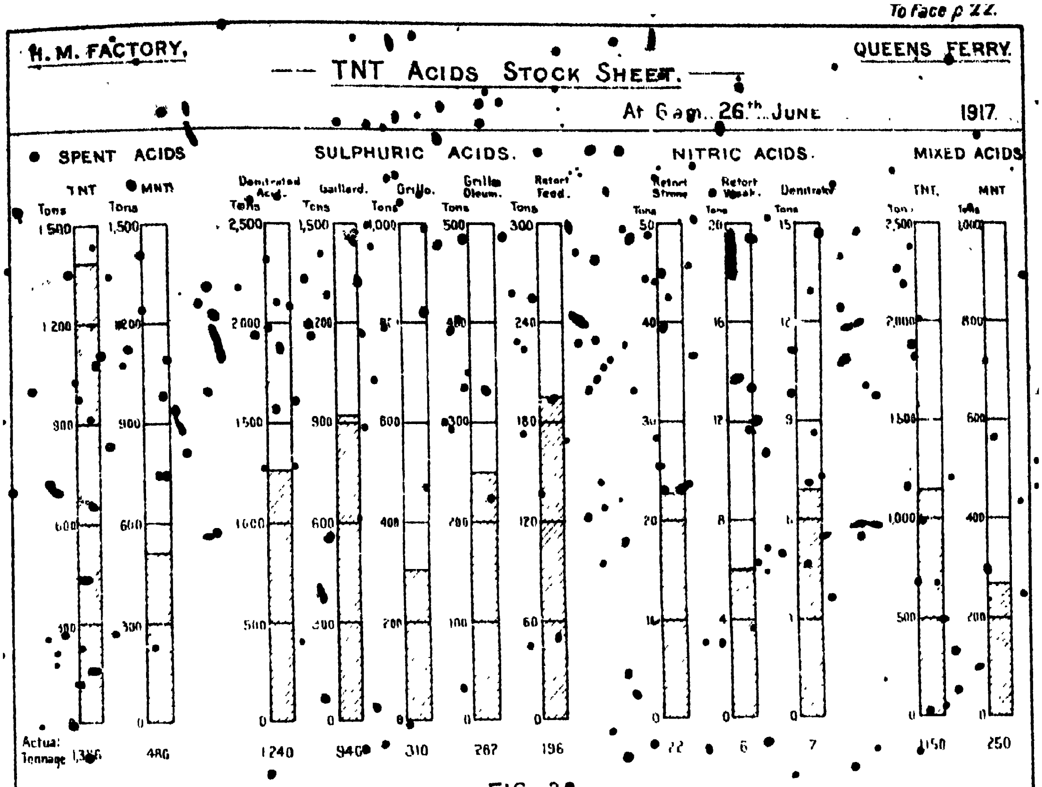

FIG. 3.

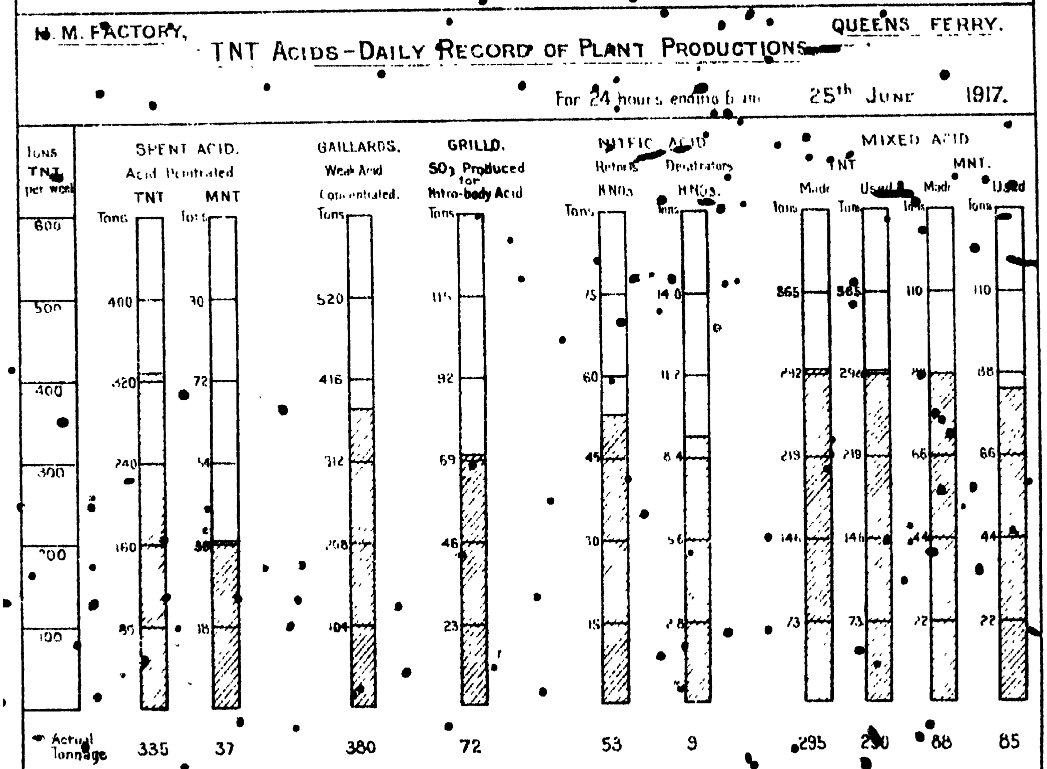

FIG. 4.

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The plant production form (Fig. 4) is based on the acid balance sheet (Fig. 2) and aims at showing the work done by each plant in the Acids Section. This can be done by giving the quantities either of the acids treated or of the acids produced, or both, but in order to keep the form as simple as possible only one operation is given, the other being inferred from it. The form might with advantage be made to indicate the daily production of finished product (in this case TNT), but as the return of this figure is made from another section of the factory, the corresponding figure given is that of the mixed acids used for mono- and trinitration, which serve as a measure of such production. The form is so arranged that horizontal lines drawn through the points on the first column marked into hundreds of tons of TNT per week will mark off on the remaining columns the daily figures required from each particular plant for this weekly production of TNT. Thus, for normal working, the ends of the shaded portions of the columns (which represent the day's work) should approximate to a horizontal line. In Fig. 4 will be seen a reproduction of the plant productions form for the 24 hours ending 6 a.m. on the 24th June 1917, at which period the plants were working to a weekly programme of 350 tons of TNT. As regards the production of SO_3 at the Grillo oleum plant, it will be noticed that this figure is less than that stipulated. This was intentional, however, in order to work off stocks of SO_3 in the spent acid.

Interpretation of Plant Returns.—The daily record of plant production (Fig. 4) is not alone sufficient to enable the production over a period to be carefully watched. A daily fluctuation in output is in many cases unavoidable, and it may be necessary, as in the case of the Gaillard concentration plant, to condense seven days' work into six days in order to leave one day for burning out the flues, &c. To keep track of these fluctuations, therefore, each item on the plant production form is entered on another form similar to that reproduced on the following page, which is a copy of that filled in for "TNT spent acid denitrated" for the week ending June 30th, 1917.

On this form the daily production figure is subtracted from the required figure, and the difference (plus or minus) entered in the adjoining column. This is then added to the excess or deficit to date, and the resulting figure is converted in the fourth column into terms of tons of TNT. This last figure, which represents the over- or under-production of each plant in terms of final product, can be shown graphically as in Figs. 5 and 6, so that the position *to date* of each portion of the Acids Section may be seen at a glance. In Fig. 5 the vertical scale represents tons of TNT, the points from which each curve starts indicating the required production of TNT. If the processes shown were exactly carried out to the programme given (*e.g.*, 350 tons of TNT per week), the lines would be horizontal, so that deviation from the horizontal shows at any time the excess or deficit in terms of tons of TNT over that quantity. In Fig. 6 the vertical scale also represents tons of TNT, but the form is set out in a similar manner to the daily production form, Fig. 4. As before, horizontal lines through the daily tonnage of TNT required (50 tons in this case) should coincide with the plant production. The deviation from the horizontal (which, as in Fig. 5, is plotted by reference to the figures in the last column of the record of plant output below) gives the excess or deficit to date in terms of TNT, or, by referring to the figures in the vertical column, of the actual tonnages of acid. An examination of either of these forms will show at once, not only which parts of the Acids Section are out of balance, but the amount of forcing or checking which is necessary. Thus, for the week illustrated, a glance at Fig. 6 shows that the under-production at the Grillo oleum plant was equivalent to 25 tons of TNT or 40 tons of SO_3; the nitric acid retorts over-production was equivalent to 10 tons of TNT or 10 tons of HNO_3; the production of MNT mixed acid was below the required figure to the extent of approximately 16 tons of TNT or 15 tons of mixed acid; and the remaining processes were carried out to schedule.

RECORD OF PLANT OUTPUT.

(Acids Section.)

For Week ending 6 a.m., *30th June* 1917.

Acid :—*TNT Spent Acid denitrated (5·6 Tons ≡ 1 Ton TNT).*

Flow sheet requirement.	Daily tonnage. *280* (350 tons of TNT per week).	Excess over weight required.	Total excess to date.	Total in terms of tons TNT.
Brought forward - -	—	—	—	—
Day ending 6 a.m.				
Sunday - - - -	*214*	*−36*	*−36*	*− 6*
Monday - - - -	*335*	*+55*	*+19*	*+ 3*
Tuesday - - - -	*325*	*+45*	*+69*	*+12*
Wednesday - - - -	*208*	*−72*	*− 3*	*0*
Thursday - - - -	*287*	*+ 7*	*+ 4*	*+ 1*
Friday - - - -	*266*	*−14*	*−10*	*− 2*
Saturday - - - -	*280*	*0*	*−10*	*− 2*

Remarks—

It will be seen that these graphs furnish the necessary data for the effective control of the acid plants individually and as a whole, *provided that the acids balance represents the actual working conditions of the plants involved.* Any departure from the stipulated strengths of acids, operating

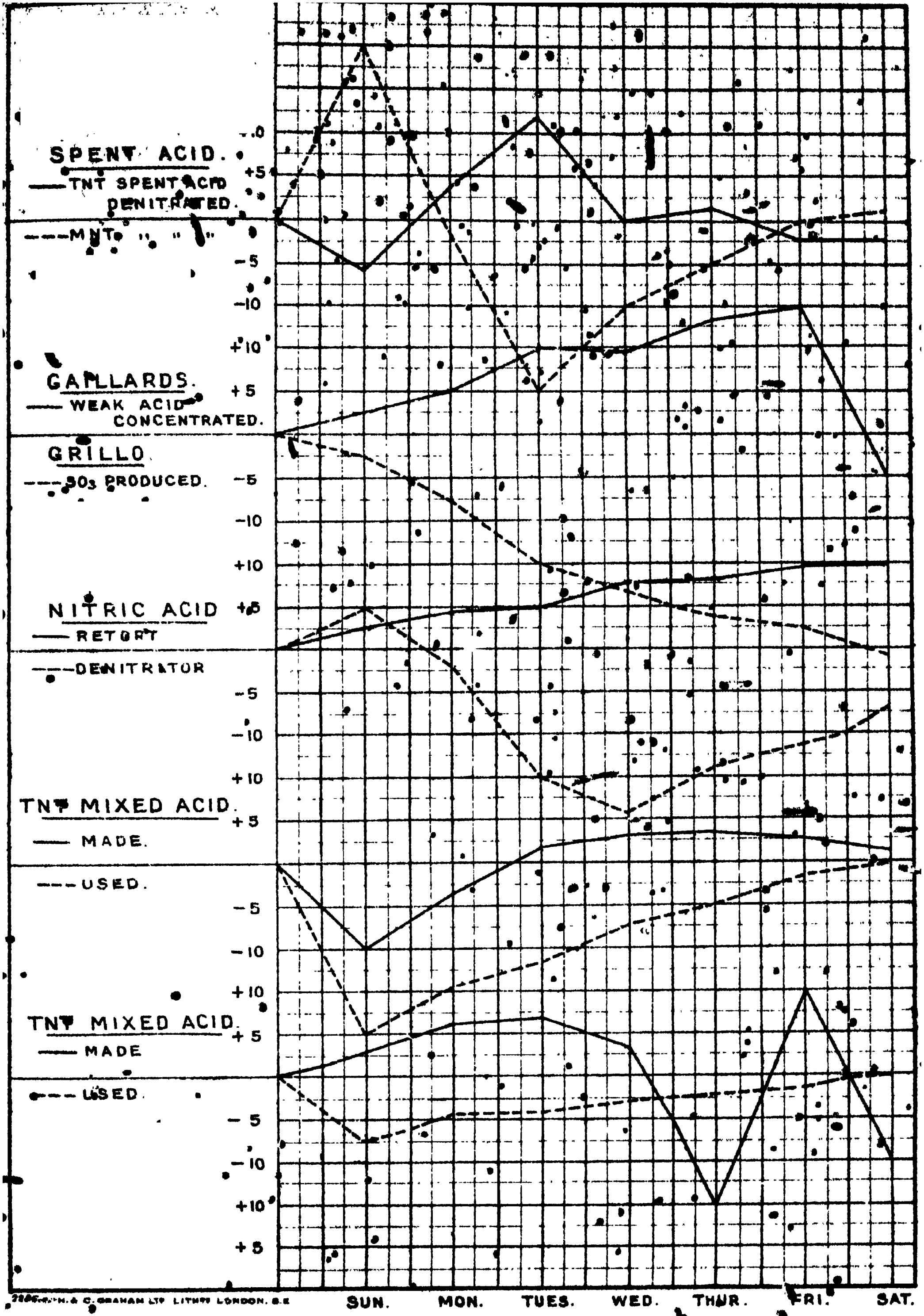

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FIG. 5.

To follow p 24

H.M. FACTORY, — TNT ACIDS WEEKLY RECORD OF PLANT PRODUCTIONS. — QUEEN'S FERRY.

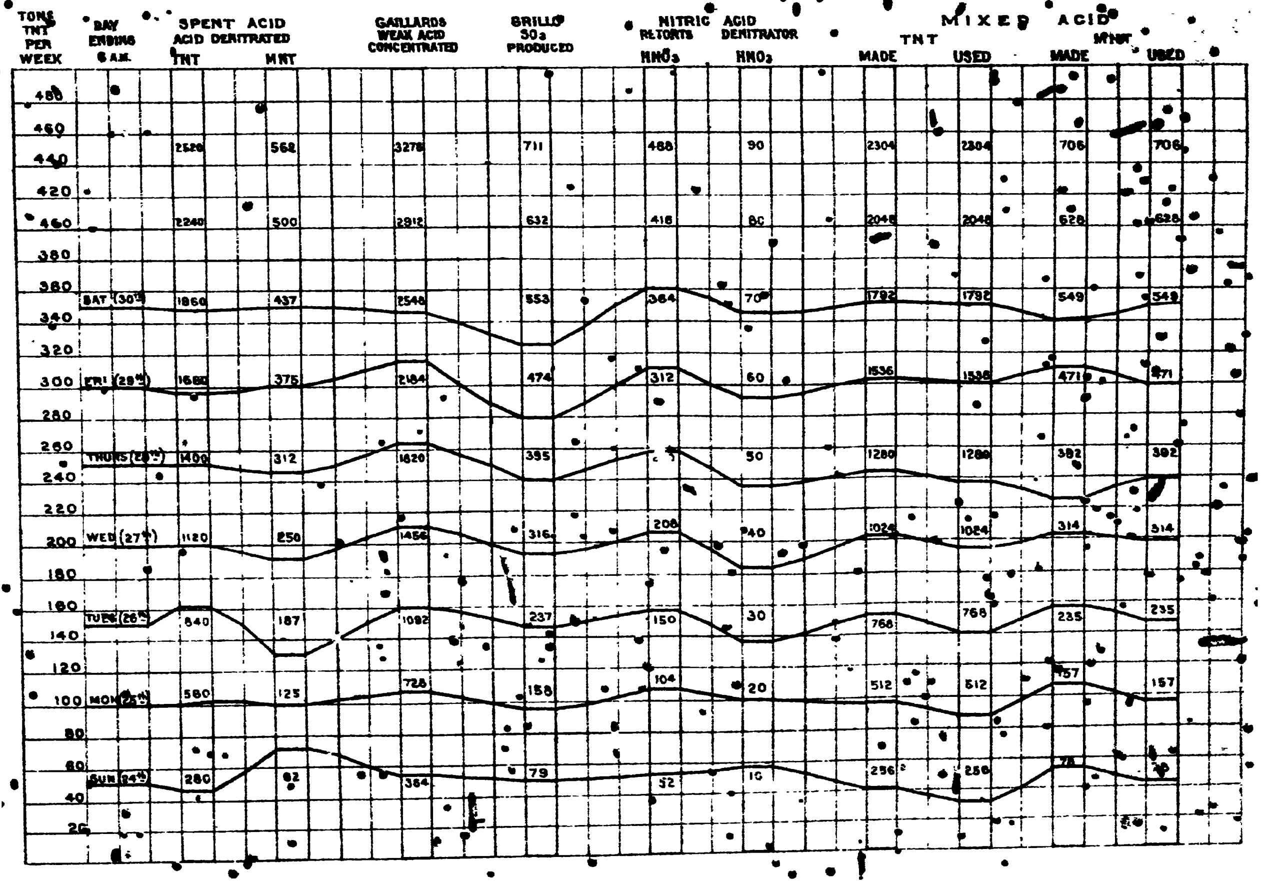

FIG. 6.

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ULTIMATE DESTINATION OF NITROGEN IN TRINITROTOLUENE MANUFACTURE.

For Period –
Oct. 27th – Dec. 1st 1917.

Basis :-
1627·01 Tons Toluene
2364·37 " MNT.
3413·74 " TNT.

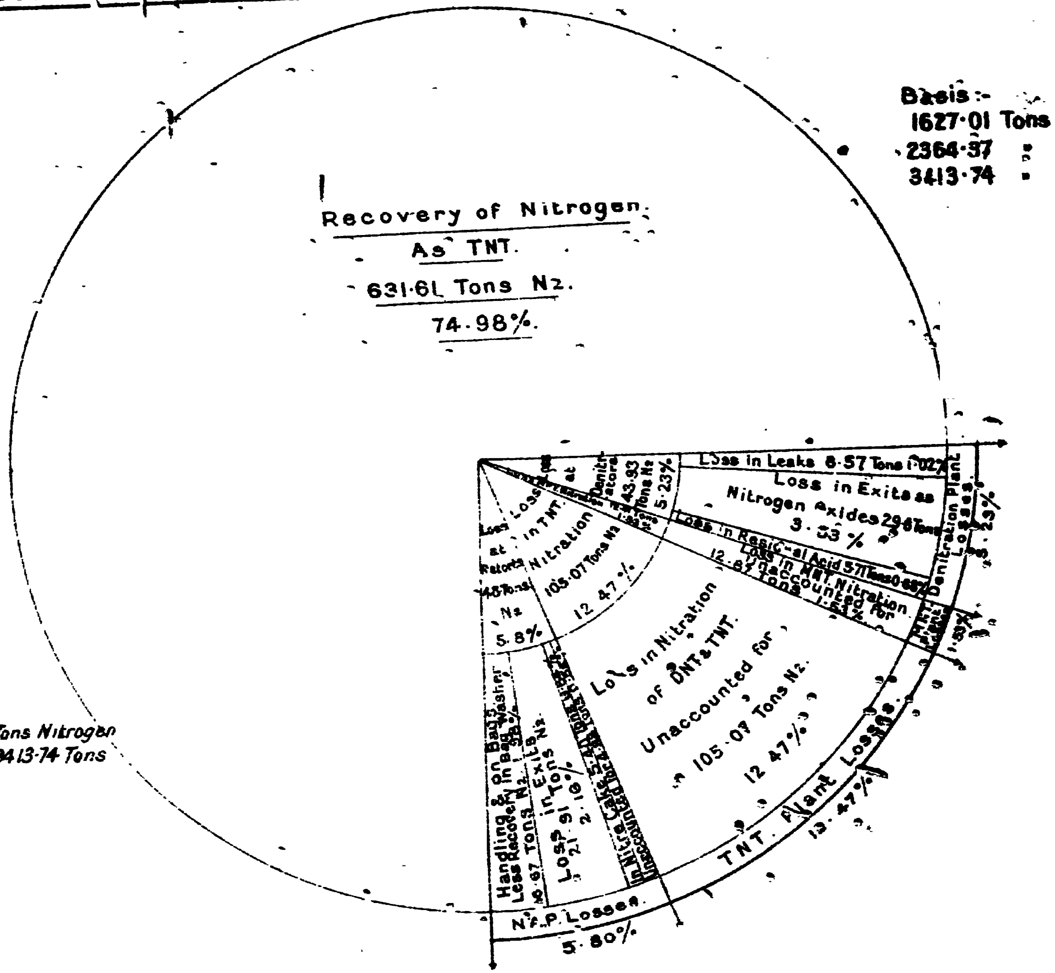

FIG 7.

Ultimate destination of 842·83 Tons Nitrogen consumed in the manufacture of 3413·74 Tons TRINITROTOLUENE.

efficiencies, acid exports, or nitration losses, &c., will upset the acids balance to a greater or less degree. It is essential, therefore, to keep closely in touch with the weekly plant reports and laboratory returns, which will disclose such changes if any are taking place, and to note any variations from previous practice which has been standardised by the acids balance. In certain cases it will be necessary to modify plant practice (*e.g.*, if 47 per cent. instead of 50 per cent. nitric acid were produced at the denitrators, or if weak sulphuric acid of 70 per cent. instead of 65 per cent. strength were issued from the Grillo scrubbing system), whilst periodically the composition of the mixed acids may be changed, in which case it will be necessary to amend or reconstruct the acids balance as a whole.

Another form of presenting summarised results of plant working is that shown in Fig. 7, which gives the ultimate destination over a certain period of nitrogen in TNT manufacture. Such charts, if systematically drawn up, have been found very useful in indicating avoidable sources of loss, and in enabling preventable waste of raw materials to be reduced to a minimum.

NITROGLYCERINE ACIDS CYCLE.

It is not proposed to give at length the construction of an acid balance for NG manufacture, as the subject bears such a close resemblance to the TNT acid cycle already described. Although the nitration process, and in fact the manufacture of NG as a whole, is dissimilar in very many respects from TNT manufacture, yet the method of preparation of mixed acids used and the subsequent treatment of the waste acid produced have much in common.

In setting out the acids balance for NG manufacture it is usual to include this along with a guncotton or nitrocellulose acids balance as shown in the acid and water balance for 700 tons per week of R.D.B. cordite, Fig. 10. A glance at this sheet will show how interconnected the two cycles are, and the desirability of treating them together, especially as regards the redistillation with sulphuric acid of the weak nitric acid resulting from the denitration of the NG and GC or NC spent acid.

GUNCOTTON AND NITROCELLULOSE ACIDS CYCLES.*

General.—The essential difference between the production of TNT and NG on the one hand and GC and NC on the other is the method of treating the spent acids resulting from the last-named manufactures. The spent acid resulting from TNT manufacture contains little or no nitric acid, the nitrogen content being almost entirely in the form of nitrous acid, which is present to the extent of 3·5 per cent. (calculated as HNO_3). NG spent acid contains nitric acid as well as nitrous acid, which are together present to the extent of about 8·5 per cent.

---

* For purposes of convenience these two explosives are taken together, as the methods used for their preparation are almost identical, the chief difference being in the composition of the mixed acids used. The term guncotton is here used as indicating the highest nitrated cellulose, which is substantially *insoluble* in ether-alcohol; nitrocellulose is generally regarded as a lower nitrated product, which is *soluble* in ether-alcohol.

(calculated as HNO_3). It is necessary to denitrate each of these spent acids by means of steam in order, in the first place, to remove or destroy any dissolved organic nitro-compounds, and secondly, to recover in a usable form the nitric and sulphuric acid which they contain,* *i.e.*, the whole of the spent acid is in each case split up into weak sulphuric acid and weak nitric acid, which after suitable treatment are then reintroduced separately into the cycle at the acid mixing plant. On the other hand, the spent acid from GC manufacture does not differ very greatly in composition from the original nitration mixture used, only a small proportion of its nitric acid content, having been replaced by water. Under the conditions of the displacement process, GC and NC are manufactured by immersing suitably prepared cotton waste in certain nitration mixtures,† and the latter during the conversion of the cotton waste into guncotton or nitrocellulose, lose nitric acid, together with a small quantity of sulphuric acid, and gain a certain amount of water. No foreign matter,‡ however, which would make the acid otherwise unfit for manufacture is introduced during the nitration operation, and it is therefore necessary only to replace the proportions of nitric and sulphuric acids which have been removed and to reduce the water content, in order to render the spent acid suitable for a further nitration cycle.

In the case of the GC or NC acids cycle, therefore, the spent acid is divided into two parts, the greater of which is "revivified," *i.e.*, brought up again to the composition of the original mixed acid by the addition of a specially prepared "regenerative" mixture rich in nitric acid and of low water content, whilst the smaller fraction of the spent acid is treated in stills for the recovery of the nitric and sulphuric acids which it contains. The nitric acid thus obtained is chiefly in the form of strong acid, but a certain amount of water is invariably driven off as the temperature of the still rises, so that the later fractions of the acid are considerably weaker than the first fractions. Since it may not be possible to utilise all the weak nitric acid on the plant, viz., that produced both at the stills and at the retorts—for acid mixing in the manufacture of nitrocellulose, it is customary to collect all the weak nitric acid which cannot be utilised for acid-mixing purposes, and to mix it with strong sulphuric acid. This mixture is then returned to the stills and the nitric acid distilled off, the bulk of the water remaining with the sulphuric acid. Since, however, any distillation of this kind will always yield a certain proportion of the nitric acid in the form of weak acid, it is obvious that there is a continual circulation of nitric acid through the stills in the process of conversion to strong nitric acid. The same consideration applies, to a certain extent, to the treatment of nitroglycerine spent acid. The denitration of this acid in the columns gives rise to a relatively weak nitric acid, which, if it cannot be utilised for acid mixing, is mixed with strong sulphuric acid, the mixture being then distilled in order to drive off the nitric acid as free as possible from water. In this operation a small quantity of weak nitric acid is again formed, which in turn must be mixed with strong sulphuric acid and redistilled. In a combined acids cycle, such as that shown in Fig. 10, it is usual to mix the excess of weak nitric acid from nitroglycerine and guncotton or nitrocellulose manufacture, and to concentrate it together, instead of separately.

---

* *See* No. 1 of this Series: "Denitration of Spent Acids."

† It is interesting to note how important it is that the composition of these mixed acids or nitration mixtures should rigidly conform to the definite limits laid down for them. In the case of TNT and nitroglycerine manufacture fairly wide limits are permissible in the composition of the nitration mixtures, since the products of nitration are definite compounds—viz., TNT and nitroglycerine—a good yield, although obviously of great importance, being less essential than uniformity in the composition of the end product. In the production of guncotton and nitrocellulose, however, far greater exactness must be observed in preparing the acid mixtures for nitration. In order to secure a product of uniform nitrogen content (which is of paramount importance from the point of view of ballistics), it is necessary to work to very clearly defined limits as regards the mixed acids used, as a slight deviation from the standard conditions reflects in a very marked manner on the degree of nitration, *i.e.*, the nitrogen content, of the nitrated product. This is especially significant in the case of the lower nitrated nitrocelluloses with nitrogen contents in the neighbourhood of 12 per cent.

‡ The gradual accumulation of acid sludge (consisting chiefly of ferric sulphate) is inevitable, which necessitates the periodical cleaning out of the spent acid settling tanks, but this factor in no way prevents the residual nitration acids from being put to further use.

The proportion of guncotton or nitrocellulose spent acid to be revivified depends upon the combined acid balance throughout the plant. A method of determining the exact measure in which nitric and sulphuric acids must be added to a guncotton spent acid in order to yield a product of standard composition is shown by the following explanation and example. In principle the same method applies to the regeneration of nitrocellulose spent acids.

Method of calculating Guncotton Acid Mixtures: Case 1.—The average composition of the spent acid usually available for making up the stock of guncotton mixed acid is as follows:—

	Per cent.
H_2SO_4	72·2
HNO_3	17·3
H_2O	10·5
	100·0

and from 75 to 80 parts of such acid are produced for every 100 parts of mixed acid used.

Now, in the ordinary course of factory practice, it is necessary to produce just as much mixed acid as that which originally produced the spent acid, *i.e.*, for every 75-80 parts, say, of spent acid it is necessary to revivify or regenerate by the addition of nitric acid and sulphuric acids such a portion as will yield 100 parts of fresh mixed acid. What portion exactly that will be depends entirely upon the strength of the nitric acid and sulphuric acids available for revivification. The nitric acid may contain from 90 to 94 per cent. of HNO_3 and the sulphuric acid from, say, 93 per cent. up to 104 per cent. of H_2SO_4 (if 20 per cent. oleum is supplied).

Let it be assumed, for example, that the factory has the following acids in stock :—

	GC spent acid.	Sulphuric acid.	Nitric acid.
	Per cent.	Per cent.	Per cent.
H_2SO_4	72·2	98	—
HNO_3	17·3	—	93
H_2O	10·5	2	7

and that it is necessary to produce 100 tons of guncotton mixed acid of the following composition :—

	Per cent
H_2SO_4	70
HNO_3	21
H_2O	9

Then, the first point to be clearly recognised is that the acids available for making up the deficiencies of spent acid are sulphuric acid of 98 per cent. and nitric acid of 93 per cent. strengths. Assuming further that no spent acid were available, and that it were necessary to make up the mixed acid direct from sulphuric and nitric acids, then 70 parts of H_2SO_4 require $\frac{70 \times 100}{98} = 71·5$ parts of 98 per cent. sulphuric acid, and 21 parts of HNO_3 require $\frac{21 \times 100}{93} = 22·6$ parts of 93 per cent. nitric acid, leaving 5·9 parts of "free" water.

The object in view, however, is not to draw entirely on fresh sulphuric and nitric acids, but to use up as much spent acid as is conveniently possible. The composition of the latter which it is desired to utilise is approximately as follows :—

	Per cent.
H_2SO_4	72·2
HNO_3	17·3
H_2O	10·5
	100·0

and in order to make up a mixed acid of this composition from sulphuric acid of 98 per cent. strength and nitric acid of 93 per cent. strength, 72·2 parts of H_2SO_4 require $\frac{72·2 \times 100}{98} = 73·7$ parts of sulphuric acid, and 17·3 parts of HNO_3 require $\frac{17·3 \times 100}{93} = 18·6$ parts of 93 per cent. nitric acid, leaving 7·7 parts of "free" water.

It will be seen, then, that if the available sulphuric and nitric acids were wholly used to make up the final mixture required, it would be necessary to add 5·9 parts of water for every 100 parts of mixed acid required; whereas, if the same acids were used to make up the spent acid, 7·7 parts of water would need to be added to give the desired composition. That is to say, if the spent acid be used for making fresh mixed acid it amounts to the same thing as using sulphuric and nitric acids of the strengths available, except that water is being added at the same time; and the amount of spent acid which can be utilised for mixing purposes is limited by the amount of water which can be added to the mixed acid. Obviously, if the spent acid contains 7·7 parts of "free" water, and it is desired that the final regenerated mixed acid should contain 5·9 parts of "free" water, then the maximum quantity of spent acid which can be utilised for every 100 parts of mixed acid is—

$$\frac{5{\cdot}9 \times 100}{7{\cdot}7} = 76{\cdot}6 \text{ parts.}$$

The final step is to determine the amounts of sulphuric and nitric acids which are to be added to the spent acid, and this part of the determination is made as follows :—

	Parts of 98 per cent sulphuric acid	Parts of 93 per cent. nitric acid	Parts of "free" water.
From the above it will be seen that 100 parts of mixed acid require -	71·5	22·6	5·9
From the spent acid are derived :—			
76·6 parts at 73·7 per cent. of 98 per cent. sulphuric acid - -	56·4	—	—
76·6 parts at 18·6 per cent. of 93 per cent. nitric acid - - -	—	14·3	—
76·6 parts at 7·7 per cent. of "free" water - - - - - -	—	—	5·9
It is therefore necessary to add -	15·1	8·3	—

To sum up, therefore, the required composition for 100 parts of G fresh mixed acid will be obtained by mixing the following :—

GC strong spent acid - - - - -	76·6	parts.
Sulphuric acid (98 per cent.) - - - -	15·1	"
Nitric acid (93 per cent.) - - - -	8·3	"
	100·0	"

The conclusion may be verified as follows :—

	H_2SO_4	HNO_3.	H_2O
76·6 parts of GC strong spent acid of composition :— H_2SO_4 72·2 per cent. HNO_3 17·3 per cent. H_2O 10·5 per cent. } contain	55·3	13·3	8·0
15·1 parts of sulphuric acid of composition :— H_2SO_4 98·0 per cent. H_2O 2·0 per cent. } contain	14·8	—	0·3
8·3 parts of nitric acid of composition :— HNO_3 93·0 per cent. H_2O 7·0 per cent. } contain		7·7	0·6
	70·1	21·0	8·9

Method of Calculating Guncotton Acid Mixtures: Case 2.—The form of calculation given above assumes that stocks of sulphuric and nitric acids are kept apart, and that they can be separately brought to the mixing tanks. In many factories, however, it is found to be a more convenient practice to blend strong nitric acid with sulphuric acid to form what is called a *revivifying acid* or *regenerating mixture*, see page 26, for a mixture of the two acids is more safely stored in large vessels than is nitric acid alone. In this case the necessary calculations take a slightly different form, for the regenerative mixture is so made that it contains a smaller proportion of sulphuric acid than is actually necessary to effect the revivification of the spent acid, leaving the exact adjustment to be subsequently made by adding sulphuric acid.

As an example, the foregoing case may be given, where in order to effect revivification it was necessary to add to each 76·6 parts of spent acid 15·1 of sulphuric acid and 8·3 of nitric acid. It would have been equally efficacious if 20·4 parts of a regenerative mixture containing 12·1 parts of 98 per cent. sulphuric acid and 8·3 parts of 93 per cent. nitric acid had been added from one storage vessel, and three parts of 98 per cent. sulphuric acid from another.

Now, in ordinary factory practice it is not possible to ensure regenerative mixtures or sulphuric acid of exactly constant composition, but this represents no complication, for it is only necessary to reduce the regenerative mixture to terms of *acids available*, and the calculation then follows the same lines as in Case No. 1. For instance, supposing the acids available are GC spent acid of the composition given above, 98 per cent. sulphuric acid, and a regenerative mixture, and it is intended to use the sulphuric acid for final adjustment; then, for purposes of calculation the regenerative mixture is reduced to terms of a mixture of 98 per cent. sulphuric acid and nitric acid, the strength of the latter being determined by calculation thus :-

A regenerative mixture gave on analysis :—

	Per cent.
H_2SO_4	58·1
HNO_3	37·9
H_2O	4·0
	100·0

and the sulphuric acid :—

	Per cent.
H_2SO_4	98·0
H_2O	2·0
	100·0

If it is assumed that the H_2SO_4 content of the regenerative mixture exists in the form of 98 per cent. acid, then the strength of the nitric acid must be :—

—	H_2SO_4.	HNO_3.	H_2O.
Regenerative mixture - - - - -	58·1	37·9	4·0
The H_2SO_4 as 98 per cent. $= \frac{58·1 \times 100}{98}$ -	58·1	—	1·2
∴ nitric acid -	—	37·9	2·8

i.e., $\frac{37·9 \times 100}{40·7}$ or 93 per cent.

Thus, the regenerative mixture contains 98 per cent. sulphuric acid and 93 per cent. nitric acid mixed in the proportion of :—

Sulphuric acid - - - - - -	59·3 parts.
Nitric acid - - - - - -	40·7 „

The necessary basis for calculation is now provided, for it is clear that to make up fresh mixed acid the following acids are available :—

—	Spent acid.	Nitric acid.	Sulphuric acid.
	Per cent.	Per cent.	Per cent.
H_2SO_4 - - - - - -	72·2	—	98
HNO_3 - - - - - -	17·3	93	—
H_2O - - - - - -	10·5	7	2

The calculation then takes the same form as in Case 1 (page 29), thus :—

—	98 per cent. sulphuric acid.	93 per cent. nitric acid.	Free water.
100 parts of mixed acid require - -	71·5	22·6	5·9
From the spent acid are derived :—			
76·6 parts at 73·7 per cent. of 98 per cent. sulphuric acid - - - - -	56·4	—	—
76·6 parts at 18·6 per cent. of 93 per cent. nitric acid - - - - -	—	14·3	—
76·6 parts at 7·7 per cent. of free water	—	—	5·9
It is therefore necessary to add - - -	15·1	8·3	—
20·4 parts of regenerative mixture contain :—			
59·3 per cent. of 98 per cent. sulphuric acid - - - - - - - -	12·1	—	—
40·7 per cent. of 93 per cent. nitric acid	—	8·3	—
Balance of 98 per cent. sulphuric acid to be added.	3·0	—	—

The required composition for the 100 parts of fresh mixed acids will therefore be obtained by mixing the following:—

GC spent acid	-	76·6 parts.
Regenerative mixture	-	20·4 „
Sulphuric acid (98 per cent.)	-	3·0 „
		100·0 „

It should be noted that in cases where the sulphuric acid available for regeneration is in the form of oleum, then the acids involved should be reduced to terms of oleum. The following calculation relating to the revivification of spent acid from the manufacture of nitrocellulose illustrates this, and forms an example of the manner in which such records should appear in the Mixing Book.

Acid Mix No......... *Nitrocellulose.*

Acid required.		Acids available.		
		Spent acid.	Oleum.	Nitric acid.
	Per cent.	Per cent.	Per cent.	Per cent.
$\mathrm{H_2SO_4}$ - - - - -	61·6	61·0	85·3 ($\mathrm{SO_3}$)	93·0
$\mathrm{HNO_3}$ - - - - -	22·4	18·7	—	—
$\mathrm{H_2O}$ - - - - -	16·0	20·3	14·7	7·0

A.

$$\frac{61{\cdot}6\ \mathrm{H_2SO_4} \times 81{\cdot}63\ (\mathrm{SO_3} \text{ in } \mathrm{H_2SO_4})}{85{\cdot}3\ (\mathrm{SO_3} \text{ in oleum})} = 59 \text{ parts of oleum.}$$

$$\frac{22{\cdot}4 \times 100}{93} = 24{\cdot}1 \text{ parts of 93 per cent nitric acid.}$$

Free water (difference) = 16·9 parts.

B.

$$\frac{61 \times 81{\cdot}63}{85{\cdot}3} = 58{\cdot}4 \text{ parts of oleum.}$$

$$\frac{18{\cdot}7 \times 100}{93} = 20{\cdot}1 \text{ parts of 93 per cent. nitric acid.}$$

Free water (difference) = 21·5 parts.

$$\therefore \frac{16{\cdot}9 \times 100}{21{\cdot}5} = 78{\cdot}6$$ parts of spent acid can be taken for each 100 of fresh mixed acid required.

	Parts of oleum (85·3 per cent. $\mathrm{SO_3}$).	Parts of 93 per cent nitric acid.	Parts of "free" water
From the above it will be seen that 100 parts of mixed acid require -	59·0	24·1	16·9
From the spent acid are derived:—			
78·6 parts at 58·4 per cent. of oleum (85·3 per cent. $\mathrm{SO_3}$) -	45·9	—	—
78·6 parts at 20·1 per cent. of 93 per cent. nitric acid - - -	—	15·8	—
78·6 parts at 21·5 per cent. of "free" water - - - -	—	—	16·9
It is therefore necessary to add -	13·1	8·3	—

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DESTINATION OF NITROGEN IN NITRO-GLYCERINE MANUFACTURE.

Month ended 27th April 1918.

		Tons Nitrogen	Percentage
Crude Nitrate Consumed		149·10	100·00
Nitrehandling loss.		1·93	1·30
Retorts losses.			
Nitre Cake.	·07	4·83	3·25
Losses at exits.	1·24		
Leaks into Condenser Water.	·28		
Fumes and general leaks.	3·24		
Denitrators losses.			
Loss in Residual Acid.	·02	·56	·38
Loss in exits	·40		
Loss due to leaks.	·12		
Unaccounted for	·02		
Loss in Nitration		5·65	3·79
Recovered in Nitro-Glycerine.		136·13	91·28
735·82 Tons N.G.		149·10	100·00

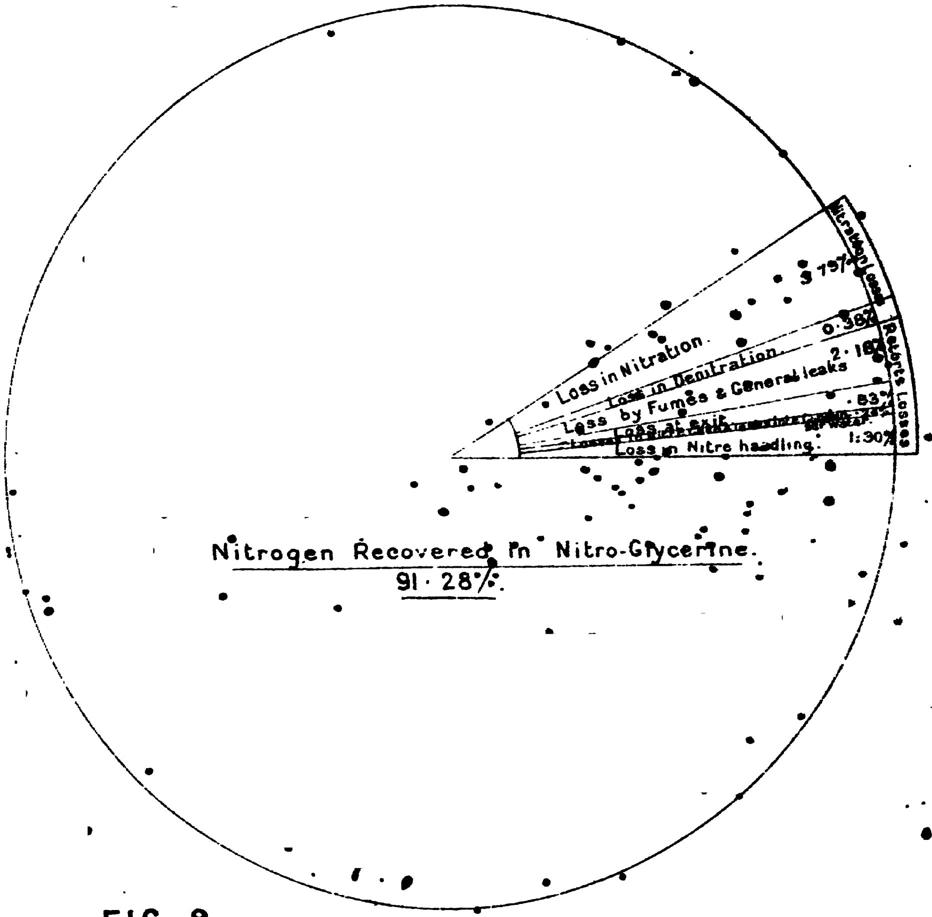

FIG. 8.

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DESTINATION OF NITROGEN IN NITRO-COTTON MANUFACTURE.

Month ended 27th April 1918.

	Tons Nitrogen.		Percentag
Crude Nitrate Consumed.		126·34	100·00
Nitre handling loss		1·63	1·29
Retorts Losses.			
Nitre Cake.	·06	4·09	3·24
Losses at exits	1·05		
Leaks into Condenser Water.	·24		
Fumes and General leaks	2·74		
Stills Losses.			
Losses in Residual Acid.	·42	6·35	5·03
Losses at exits	5·33		
Leaks and drips	·60		
Mixing Losses.			
Nitrating House Losses			
Waste Burnt	·05	22·18	17·26
Nitrating House drains	20·25		
Fumes etc.	·17		
Vat House losses.	1·34		
Recovered in finished Nitro-Cotton.		92·09	73·18
754·80 Tons N.C.		126·34	100·00

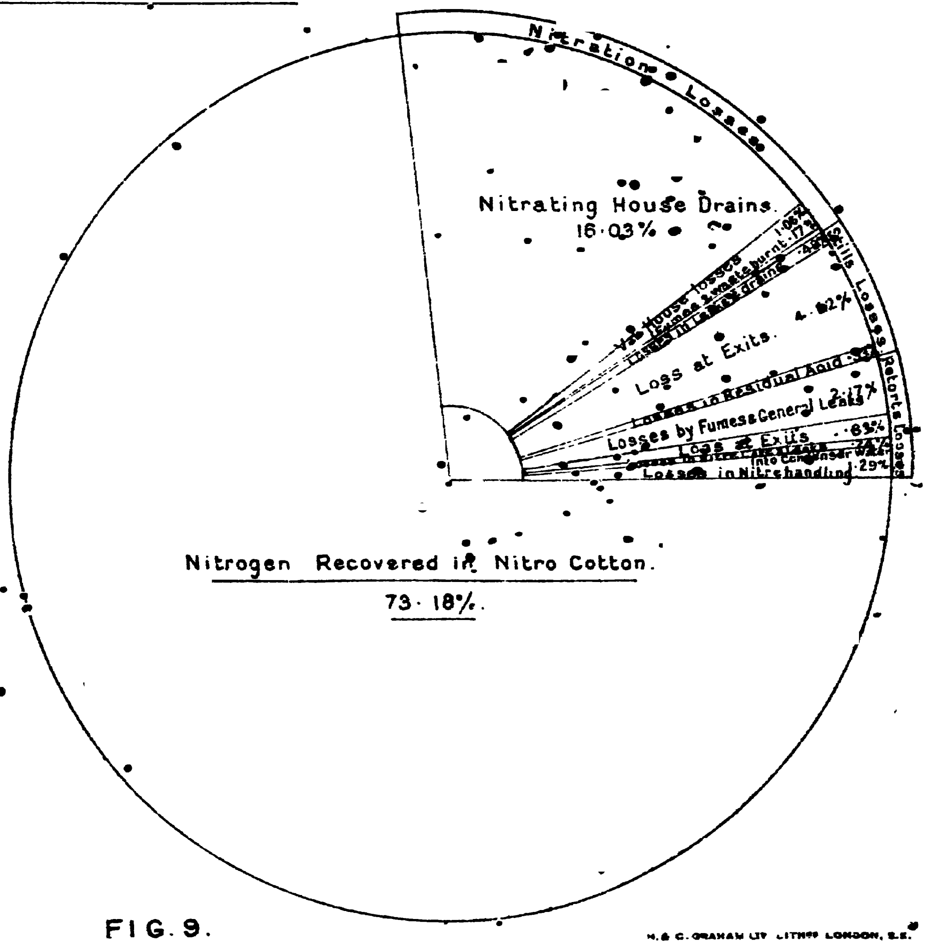

FIG. 9.

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To sum up, therefore, the required composition for 100 parts of NC fresh mixed acid will be obtained by mixing the following :—

NC spent acid	78·6 parts.
Oleum (85·3 per cent. SO_3)	13·1 ″
Nitric acid (93 per cent.)	8·3 ″
	100·0

Charts giving the ultimate destination of nitrogen in the production of nitroglycerine and nitrocellulose are shown respectively in Figs. 8 and 9, and a combined acids balance for nitroglycerine and nitrocellulose acids in the manufacture of R.D.B. cordite is reproduced in Fig. 10.

SECTION 2.

THE POSITION OF THE ACID MIXING PLANT IN THE ACIDS CYCLE, AND THE PROCEDURE ADOPTED IN MIXING.

General.—This section records some of the work done and the results and methods arrived at on the TNT acid mixing plant at H.M. Factory, Queen's Ferry, and it is hoped that the subject-matter may prove useful to chemists and others who may be responsible for any part of the work in connection with acid mixing. The subject has been treated in considerable detail, the object throughout being to render the actual practice of acid mixing as explicit as possible.

The position of the TNT Acid Mixing Plant in the Acids Cycle.—The work of the TNT acid mixing plant must first of all be considered in relation to the TNT acids cycle, a specimen of which is reproduced in Fig. 11. The function of the mixing plant in the acids circulation is twofold, viz.:—

(*a*) To keep the nitration plant supplied with mixed acids of definite composition.

(*b*) To utilise the available acids in the most economical way. From the acid cycle it is clear that the following acids are available for mixing purposes:—

(a) *Sulphuric Acids.*

(1) Oleum from Grillo plant (105 per cent. H_2SO_4).

(2) Sulphuric acid from Grillo plant (98·6 per cent. H_2SO_4).

(3) Sulphuric acid from Gaillard concentrators (90 per cent. H_2SO_4).

(4) TNT spent acid (91 per cent. H_2SO_4).

Spent acid is not shown on the flow-sheet as being available for mixing, but a spent acid line to the mixers exists, and spent acid is available for doping when absolutely necessary.

(b) *Nitric Acids.*

(1) Retort strong nitric acid of 86 per cent. HNO_3 average strength. This is composed of two separate acids, viz., the bulk of nitric acid of 88 per cent. strength collected from the retorts, and a much smaller quantity consisting of 50–55 per cent. nitric acid from the absorption towers.

(2) Denitrator weak nitric acid of 50 per cent. average strength.

The significance of the Acids Balance to the Mixing Plant.—The acids balance represents for the mixing plant an ideal to which it is expected to approximate as closely as possible. It is founded, of course, on past

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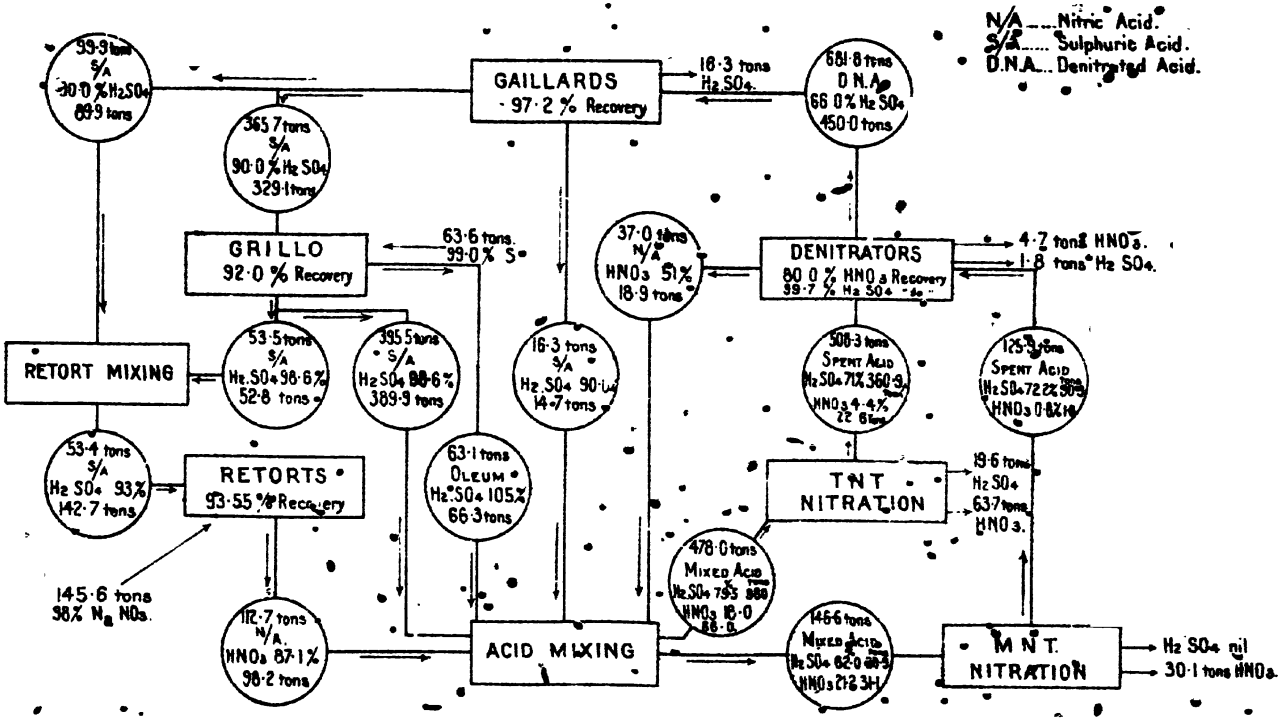
ACID BALANCE FOR 100 TONS T.N.T.


N/A.....Nitric Acid.
S/A..... Sulphuric Acid.
D.N.A... Denitrated Acid.
99·9 tons S/A 90·0 % H2SO4 89·9 tons
GAILLARDS · 97·2 % Recovery
18·3 tons H2 SO4.
681·8 tons D.N.A. 66·0 % H2 SO4 450·0 tons
365·7 tons S/A 90·0 % H2 SO4 329·1 tons
GRILLO 92·0 % Recovery
63·6 tons. 99·0 % S
37·0 tons N/A HNO3 51% 18·9 tons
DENITRATORS 80·0 % HNO3 Recovery 99·7 % H2 SO4 "do"
4·7 tons HNO3.
1·8 tons H2 SO4.
RETORT MIXING
53·5 tons S/A H2 SO4 98·6 % 52·8 tons
395·5 tons S/A H2 SO4 98·6 % 389·9 tons
16·3 tons S/A H2 SO4 90·[illegible] 14·7 tons
508·3 tons Spent Acid H2 SO4 71% 360·9 tons HNO3 4·4% 22·6 tons
125·9 tons Spent Acid H2 SO4 72·2% 90·9 tons HNO3 0·8% 1·0
53·4 tons S/A H2 SO4 93% 142·7 tons
RETORTS 93·55 % Recovery
63·1 tons Oleum H2 SO4 105% 66·3 tons
TNT NITRATION
19·6 tons H2 SO4
63·7 tons HNO3.
145·6 tons 98% Na NO3.
478·0 tons Mixed Acid H2 SO4 79·5 % 380 tons HNO3 18·0 86·0
112·7 tons N/A. HNO3 87·1% 98·2 tons
ACID MIXING
146·6 tons Mixed Acid H2 SO4 62·0 % 90·9 tons HNO3 21·2 % 31·1
M N T. NITRATION
H2 SO4 nil
30·1 tons HNO3.

— SUPPLEMENTARY NOTES. —

1. Grillo recovery - 92·0 % in Absorbers (to T.N.T. Cycle) and 3·0 % in Scrubbers (to Nitrocellulose Cycle).
2. 100 tons T N T require 1 Grillo Unit on 71·5 lbs. Sulphur Charge for 7 days.
3. VARIATION of GAILLARD CONCENTRATION FIGURE.
   - (a) Raise 0·1% for every 1·0% increase in dilution of Denitrator N/A
   - (b) Raise 0·25% for every 1·0% increase in dilution of Retort N/A.
   - (c) " 0·5% for 1 week to eliminate water in 100 tons Oleum introduced into system from without.
   - (d) Raise 0·9 % for 1 week to eliminate water in 100 tons Spent Acid taken into system.

(c) and (d) are on basis of 600 tons TNT per week.

FIG. 11.

practice and will in general hold for future working. The person in control of the acid mixing will find variations absolutely necessary from time to time, however, and these will be due chiefly to—

(*a*) Improvements or changes in the efficiency of plant working, particularly as regards the nitric acid plants.

(*b*) Variations through one cause or another in the amount of water taken in at the retorts or denitrators, as shown in the strengths of the nitric acid produced.

(*c*) Accidents in mixing; *e.g.*, a sudden increase in the dilution of a blend through water from a leaking coil entering the mixed acid undetected.

(*d*) Accidental occurrences at other plants involved in the acids cycle. For instance, during the temporary and unavoidable closing down of the denitration plant for a day or two, the storage room for spent acids may become completely filled up, and to keep the acid cycle working it would then be necessary to mix spent acid with oleum as a temporary expedient. This would naturally increase the amount of water in the cycle, which must later be removed by raising the concentration figure at the Gaillard concentrators.

Classes of Acids to be used.—It is necessary at the outset for the mixing plant to distinguish between three distinct classes of acids, viz.:—

(*a*) *Acids which must be mixed off immediately.*—To this class belong all varieties of nitric acid. Whatever their strength may be, they must be introduced into the acids circulation. The sole exceptions have been in the few isolated cases when absorber or denitrator nitric acid has been run off at a specific gravity below 1·300; the difficulty of compensating for this excess of water, and the danger to the mixer cooling coils which is involved, have precluded the use of such acid. Such cases, however, are very exceptional.

(*b*) *Acids to be used only under exceptional circumstances.*—These include—

(1) Spent acid,* the use of which must always interfere with the acids balance. Before proceeding any further, the actual effect of this will be considered.

Spent acid of 71 per cent. would, after denitration and concentration in the ordinary course of events, be issued from the Gaillards at about 91 per cent. If the effect of using 1 ton of spent acid be considered, this contains—

H_2SO_4	0·71 ton
H_2O	0·29 ,,
	1·00 ,,

The amount of H_2O in union with 0·71 ton of H_2SO_4 in 91 per cent. acid is—

$$\frac{0{\cdot}71 \times 9}{91} = 0{\cdot}07 \text{ ton.}$$

---

* These remarks do not, of course, apply to processes in which the use of revivified spent acid forms part of the original nitration scheme.

∴ Excess of water in the system due to the use of 1 ton of spent acid = 0·22 ton.

On the basis of a production of 600 tons of TNT per week, the Gaillard towers concentrate about 2,900 tons of 91 per cent. acid per week.

Now, raising the concentration figure at the Gaillard towers by 0·1 per cent. is equivalent to driving out 2·9 tons of water, and from the above it is seen that the use of 1 ton of spent acid necessitates the removal of 0·22 tons of extra water at the Gaillard towers.

∴ The amount of spent acid equivalent to an extra concentration of 0·1 per cent. at the Gaillard towers for one week $= \frac{2\cdot9}{0\cdot22} = 13$ tons, and this figure must be noted in order to preserve a correct acid balance.

(2). Weak nitric acid from the denitrators and absorbers for TNT mixed acid.

From the abstract point of view of the acids cycle, it does not make any difference whether the weak nitric acid is mixed off as MNT or TNT mixed acid. It is manifestly impossible, however, to introduce any large quantity of weak nitric acid into a TNT mixed acid, of as low a dilution as 2·7 per cent. For this reason, it is not possible to stop or materially to reduce the rate of making MNT mixed acid at any time unless adequate storage accommodation for weak nitric acid is provided.

The objections to using a limited amount of weak nitric acid (50 per cent.) for TNT mixed acid are the large amount of oleum which would be required to take up the water (this would disturb the balance of oleum, and 98·6 per cent. sulphuric acid at the Grillo plant) and the much heavier burden which would be thrown on the cooling capacity of the mixing plant.

(c). *Acids to be used as required.*—This class includes the varieties of sulphuric acid, viz., oleum, 98·6 per cent. sulphuric acid from the Grillo plant, and concentrated acid from the Gaillard towers.

The standard sulphuric acid in use is the Grillo 98·6 per cent. acid, Gaillard tower acid being used to dilute the Grillo acid when a weaker acid is needed, and oleum being used when the reverse is the case.

MNT mixes require a slightly weaker class of acid than 98·6 per cent., and the acids utilised should therefore consist chiefly of Grillo and Gaillard sulphuric acids. The utilisation of oleum and weak sulphuric acid in the same blend is generally a confession of failure or accident in mixing.

TNT mixes require an acid of greater strength than 98·6 per cent., and in this case a mixture of oleum and Grillo 98·6 per cent. acid is used. Weak sulphuric acid from the Gaillard towers should not be used as a rule, except in small quantities for doping purposes.

Oleum and Grillo 98·6 per cent. Sulphuric Acid in practice.—The statement in the last paragraph requires a slight modification. According to the acids balance, oleum and Grillo 98·6 per cent. acid are forthcoming in the exact quantities required for mixing purposes. In practice, however, it is most satisfactory to produce the oleum slightly in excess, whilst keeping the total SO_3 produced at the Grillo plant true to the requirements of the cycle. This excess of oleum accumulates and must be worked off periodically. This is accomplished by deliberately mixing off oleum with Gaillard weak acid, in connection with either (*a*) the mixing of the TNT mixed acid, or (*b*) feed acid for the nitric acid retorts, oleum being used instead of 98·6 per cent. sulphuric acid to strengthen the Gaillard weak sulphuric acid.

The Mixed Acids.—As already pointed out in Section 1, these are as follows :—

	TNT mixed acid.	MNT mixed acid.
	Per cent.	Per cent.
H_2SO_4 - - - - - - - -	$79{\cdot}5 \pm 0{\cdot}3$	$62{\cdot}0 \pm 0{\cdot}3$
HNO_3 - - - - - - - -	$17{\cdot}8 \pm 0{\cdot}3$	$21{\cdot}0 \pm 0{\cdot}3$
H_2O - - - - - - - -	$2{\cdot}7 \pm 0{\cdot}2$	$17{\cdot}9 \pm 0{\cdot}3$

TNT Mixed Acid.

TNT mixed acid in the past has been mixed to the following analyses :—

H_2SO_4	HNO_3	H_2O
Per cent.	Per cent.	Per cent.
(1) 78·4	17·0	4·6
(2) 78·5	17·25	4·25
(3) 79·5	17·8	2·7

The first of these represented, during a temporary shortage of oleum, a mixed acid of the highest dilution permissible. The chief danger in mixing this acid was in the dilution, which, with the 0·3 limit allowed, was on occasion as high as 4·9 per cent. This figure is too high for either rapid or complete nitration, to secure which it is essential that the ratio $\frac{H_2SO_4}{H_2O}$ at the end of the nitration should be greater than $\frac{91}{9}$. This ratio decreases very rapidly with increase in the dilution of the fresh mixed acid. It is lowest for the greatest dilution, viz., with a mixed acid containing

$$78{\cdot}1 : 17{\cdot}0 : 4{\cdot}9.$$

Assuming that of the 17·0 per cent. of HNO_3 13·0 per cent. is utilised and the remainder is reduced to nitrous acid, then 13·0 of HNO_3 is replaced by $\frac{18}{63} \times 13{\cdot}0 = 3{\cdot}7$ of H_2O.

$\therefore$ Total H_2O at end of nitration $= (4{\cdot}9 + 3{\cdot}7) = 8{\cdot}6$. Ignoring the nitrous acid, the ratio $\frac{H_2SO_4}{H_2O}$ at the end point of nitration is therefore $\frac{78\cdot 1}{8\cdot 6} = \frac{81\cdot 5}{9}$, which is too low, and trouble was frequently experienced in obtaining the required setting point of the nitrated product.

The next composition suggested for the mixed acid was :—

	Per cent.
H_2SO_4	78·50 ± 0·5
HNO_3	17·25 ± 0·25
H_2O	4·25 ± 0·25

and the extreme case for this acid was an analysis showing H_2SO_4 78·0 per cent., HNO_3 17·5 per cent., H_2O 4·5 per cent. Assuming 13·5 of the HNO_3 to be utilised, this would be replaced by $\frac{18}{63} \times 13\cdot 5 = 3\cdot 9$ of H_2O. The ratio $\frac{H_2SO_4}{H_2O}$ at the end point of the reaction is therefore

$$\frac{78\cdot 0}{4\cdot 5 + 3\cdot 9} = \frac{78\cdot 0}{8\cdot 4} = \frac{83\cdot 6}{9}, \text{ which is still too low.}$$

The last composition used, viz., 79·5 : 17·8 : 2·7, has as its limiting case 79·2 : 17·8 : 3·0, and the ratio $\frac{H_2SO_4}{H_2O}$ at the end point of the reaction is $\frac{79\cdot 2}{3\cdot 0 + 4\cdot 0} = \frac{79\cdot 2}{7\cdot 0} = \frac{101\cdot 8}{9\cdot 0}$.

The adoption of this mixed acid has rendered possible a very rapid attainment of the desired setting-point of TNT, with increased steadiness in working, as well as diminution of HNO_3 losses through reduction of HNO_3 to HNO_2 during the nitration process. That which is apparently but a slight change in dilution, *i.e.*, from 4·6 per cent. to 2·7 per cent., has had the following results as regards the acid mixing plant :—

(*a*) The development of much more heat during the mixing process, on account of the necessity for using oleum as one of the sulphuric acids required.

(*b*) In cases where doping with oleum is rendered necessary on account of too high a dilution, as shown by the first analysis, the oleum dope necessary to compensate for the water is increased in amount by 25 per cent.

This is evident from the following line of reasoning. The amount of oleum required for doping to reduce dilution is directly proportional to the excess in dilution, and roughly inversely proportional to the difference in dilution between the oleum (considered as having a negative dilution) and the mixed acid required. When the required dilution is 4·6, the oleum dope (with oleum of 105·0 per cent. H_2SO_4, *i.e.*, containing 85·7 per cent. of SO_3) for a given error in dilution is proportional to

$$\frac{1}{5\cdot 0 + 4\cdot 6} = \frac{1}{9\cdot 6}.$$

When the dilution required is 2·7, however, the oleum dope is proportional to—

$$\frac{1}{5\cdot0+2\cdot7}=\frac{1}{7\cdot7}.$$

In the second case, the size of the necessary dope is increased in the ratio $\frac{9\cdot6}{7\cdot7}=1\cdot25$, an increase of 25 per cent.

A further reduction in the specified dilution of TNT mixed acid would mean a still greater oleum dope for an equal error on the high side in dilution.

MNT Mixed Acid.

This has been made at various times to conform to the following limits:—

	H_2SO_4	HNO_3.	H_2O.
	Per cent.	Per cent.	Per cent.
(1)	62·0	21·0	17·0
(2)	66·5	11·5	22·0
(3)	64·0	16·0	20·0

The first of these has now been reverted to, the second and third being analyses of MNT mixed acids made by revivifying TNT undiluted spent acid.* The main objections to the last two were—

(1) The impossibility of revivifying a sufficiently large amount of spent acid, and at the same time using up the necessary amount of weak nitric acid recovered at the denitrators.

(2) The danger through corrosion to the mixing and blending plants of overstepping the dilution during the process of mixing. Some corrosion certainly did take place whenever the dilution reached 22 per cent., and the wear and tear on the cooling coils was much increased.

The important point in determining a suitable composition for MNT mixed acid is the dilution of the spent acid at the completion of the nitration process. The latter should yield a spent acid suitable for denitration. This should be as near as is safe to 70 per cent., say 71 per cent., in order to avoid the waste of steam which would be required to dilute to the 70 per cent. strength which is necessary for denitration to take place.

Taking the analysis H_2SO_4 62·0 per cent., HNO_3 21·0 per cent., H_2O 17·0 per cent., and assuming that all the HNO_3 is utilised in the nitration process, then 21·0 of HNO_3 is replaced by $\frac{18}{63} \times 21\cdot0 = 6\cdot0$ of H_2O, and the ratio $\frac{H_2SO_4}{H_2O} = \frac{62\cdot0}{17\cdot0 + 6\cdot0} = \frac{62\cdot0}{23\cdot0}$, yielding a spent acid containing 73 per cent. of H_2SO_4, which represents the limit of safety for storage in steel tanks and delivery through wrought-iron pipe lines.

---

* The quantity of dilution water added at the various stages of the trinitration process was for a time diminished in order to produce a spent acid of higher H_2SO_4 content, which might be revivified for use as a mixed acid for the mononitration stage. This procedure, although the custom in several other factories, was afterwards abandoned at Queen's Ferry. (*See* No. 2 of this Series.)

THE CALCULATION OF MIXES.

The place of a Sulphuric Acid Dope in mixing.—The difficulty of obtaining a blend of correct analysis without doping, when working with acids the composition of which is not known to within 0·1 or 0·2 per cent., is indicated by the following facts:—

(*a*) The limit of ± 0·3 per cent. allowed in the composition of the mixed acid demands accuracy in running in charges of sulphuric acid to within ⅛ inch.

(*b*) The strength of each variety of sulphuric acid used must be known to within 0·4 per cent., assuming no error during the running in of the acid.

(*c*) The strength of the nitric acid must be known to within 1·5 per cent.

(*d*) The nitric acid run in for every charge must be correct to ¼ inch.

With a mixing plant working slowly, with picked workers and thorough analysis of the acids used, it would be a comparatively easy matter to mix correctly the first time, but when a plant is working to its utmost capacity it is not possible to secure the necessary accuracy, particularly in the case of the nitric acid, which is measured in the lead receivers at the retort houses. Furthermore, each acid analysis will represent a large bulk of acid not always or necessarily of uniform strength.

Assuming, then, that a dope will usually be necessary, it pays to choose the dope which is simplest or quickest in the making, and, if possible, the one which is least liable to error. A sulphuric acid dope fulfils these conditions. It avoids the necessity of making a mix containing nitric acid, and both strength and quantities are more readily determined in the case of sulphuric acid than in the case of nitric acid.

In conclusion, it is clear that the errors mentioned above as permissible in a mix can be multiplied by "*n*" in a dope, where—

$$n = \frac{\text{blend}}{\text{dope}},$$

so that even if it were possible to mix correctly for the first analysis, there is an advantage in doping, in that the limits allowed for deviation can thereby be narrowed.

As regards Queen's Ferry practice, more correct results have been obtained by means of a dope consisting entirely of sulphuric acid and oleum than with one made up of sulphuric and nitric acids.

TNT Mixed Acid.—The TNT acid mixing plant at H.M. Factory, Queen's Ferry, comprises seven *preliminary mixing tanks* or "*mixers*," 10 feet diameter × 5 feet deep, and four *blending tanks* or "*blenders*," 20 feet diameter × 12 feet deep. These are described in detail in Section 3.

TNT mixed acid is mixed by the blend, each blend consisting of 8 feet 9 inches of mixed acid as measured by "dip" in the blender. This, together with the 34 inches remaining in the blender after each pumping, gives a total dip of 9 feet.

As stated above, blends are calculated so as to require only a sulphuric acid dope, in order to bring the mixed acid to the desired composition, *i.e.*, the HNO_3 content is calculated on the high side. For a final analysis of H_2SO_4 79·5, HNO_3 17·8, H_2O 2·7, it is customary to calculate a blend of preliminary analysis about 78·3 : 19·0 : 2·7, which can be doped with 97·3 per cent. sulphuric acid (*i.e.*, of 2·7 per cent. dilution).

TNT mixed acid is made up entirely from retort strong nitric acid, oleum, and 98·6 per cent. sulphuric acid. During the early period of the factory's working, the retorts produced practically three strengths of acid, *viz.* :—

(*a*) Strong nitric acid from the retorts of approximately 92 per cent. strength.
(*b*) Weak nitric acid from the retorts of about 70 per cent. strength.
(*c*) Weak nitric acid from the absorption towers of approximately 65 per cent. strength.

At that time, however, the recovery of nitric acid at the denitrators was low, and the 70 per cent. nitric acid from the retorts could be utilised readily along with the nitric acid from the retort absorbers and the denitrators for making MNT mixed acid. But, as the recovery at the denitrators rapidly approached its maximum, it was not possible to deal with more weak nitric acid in the MNT mixed acid than was produced at the denitrators and retort absorbers. For this reason, and also for convenience in other directions, all the acid from the retorts was run together into the lead receivers, giving an average strength of about 88 per cent. At the same time, the maximum permissible strength of the absorber acid was reduced to 50 per cent., as in the case of the denitrator nitric acid, in order to increase the nitric acid recovery at the retorts. Since these alterations, therefore, the TNT mixed acid has been made up of this 88 per cent. strong nitric acid, 98·6 per cent. sulphuric acid, and oleum. The method of calculating mixes is to determine—

(*a*) The strength of the sulphuric acid which must be mixed with the strong nitric acid available to yield TNT mixed acid of the required composition.
(*b*) The requisite amounts of oleum and 98·6 per cent. sulphuric acid to give sulphuric acid of this strength.

The actual calculation, then, is as follows:—

Each blend has a dip of 8 feet 9 inches in the blender, which is equivalent to 140·4 tons of TNT mixed acid.

140·4 tons of acid of composition H_2SO_4 78·3 per cent., HNO_3 19·0 per cent., and H_2O 2·7 per cent., require:—

$$140{\cdot}4 \times 0{\cdot}783 = 109{\cdot}93 \text{ tons of } H_2SO_4.$$
$$140{\cdot}4 \times 0{\cdot}190 = 26{\cdot}67 \text{ tons of } HNO_3.$$

Amount of strong nitric acid (88 per cent.) required to give the necessary HNO_3 content $= \frac{26{\cdot}67 \times 100}{88} = 30{\cdot}31$ tons.

Weight of sulphuric acid to be mixed with the strong nitric acid $= 140{\cdot}4 - 30{\cdot}31 = 110{\cdot}09$ tons, and the strength of the sulphuric acid which must be used for this purpose will therefore be $\frac{109{\cdot}93 \times 100}{110{\cdot}09}$ $= 99{\cdot}86$ per cent.

	Per cent.		Per cent.
Assuming oleum available at -	105·00	Difference =	5·14
Required—sulphuric acid at - -	99·86		
Assuming sulphuric acid available at	98·60	" =	1·26
		Total difference =	6·40

$\therefore$ Amount of oleum required $= \frac{110{\cdot}09 \times 1{\cdot}26}{6{\cdot}4} = 21{\cdot}68$ tons, and the amount of 98·6 per cent. sulphuric acid required $= 110{\cdot}09 - 21{\cdot}68 = 88{\cdot}41$ tons.

In order to increase the mixing capacity of the plant and to decrease the duty of the preliminary mixers, a portion of the Grillo 98·6 per cent. sulphuric acid is run direct into the blenders. For each blend five mixes are made in the preliminary mixers, each as follows:—

(1) A minimum charge of Grillo 98·6 per cent. sulphuric acid is first run in, *i.e.*, 34½ inches, this being the level of the top of the mixing cylinder, *see* page 66. Under no circumstances whatever is nitric acid added to a sulphuric acid charge of less than 34½ inches.

(2) One-fifth of the required charge of strong nitric acid is added to the sulphuric acid charge.

(3) After the contents of the mixer have been properly mixed and cooled, a portion is pumped away in two operations sufficient to allow room for the addition of one-fifth of the oleum required for the blend.

Thus, as 34½ inches of Grillo 98·6 per cent. sulphuric acid represent 11·17 tons, each mix consists of:—

11·17 tons of Grillo, 98·6 per cent. sulphuric acid.
6·06 tons of 88 per cent. nitric acid.
4·34 tons of oleum.

The oleum and strong nitric acid are thus wholly accounted for, but of the Grillo 98·6 per cent. sulphuric acid the amount in the mixes is 11·17 × 5 = 55·85 tons. The amount to be added to the blender, therefore, is 88·41 — 55·85 = 32·56 tons, or 2 feet 0¼ inches by dip in the blender. This is added last, when the five mixes have been pumped over to the blender, 98·6 per cent. sulphuric acid being run direct into the blender to bring the total dip up to 9 feet. The rise in temperature in the blender due to this addition is about 3° C., which is inconsiderable.

The distinctive features of this method of mixing are :—

(a) The high HNO_3 content of the preliminary blend.

(b) The addition of the Grillo 98·6 per cent. sulphuric acid direct to the blender.

(c) The addition of oleum to the preliminary mix of 98·6 per cent. sulphuric acid and strong nitric acid.

The alternatives to the last-mentioned procedure are either to make a preliminary mix of 98·6 per cent. sulphuric acid and oleum, to which the strong nitric acid is added, or to make special mixes of oleum and strong nitric acid. The objection to a preliminary mix of oleum and 98·6 per cent. sulphuric acid is that considerable local heat would develop at the surface of contact of the two acids. This would persist until the mixing level of 34½ inches was attained, and would cause considerable damage to the lead cooling coils. The objections as regards making mixes of oleum and strong nitric acid are :—

(1) The corrosive effect of hot oleum on the lead cooling coils.

(2) The difficulty of keeping the temperature low when a large bulk of oleum is diluted, as it would be if any strong nitric were added directly.

It is a much simpler matter to control the temperature when the oleum is added gradually to the otherwise completed mix.

Correction of the Mix for Dilution Errors.

The calculated quantities only hold provided the strengths of the acids remain as postulated. In practice, it is sufficient to modify the mixes according to the varying dilution of successive blends. The dilution may do one of two things :—

(1) It may vary round about 2·7 per cent., in which case, provided the variation is not abnormal, the problem of doping is quite simple.

(2) It may remain fairly steady at a dilution above or below 2·7 per cent. A simple calculation gives a quick method of dealing with such cases. All that has to be done is to replace a certain amount of oleum in the mixes with 98·6 per cent. sulphuric acid, or *vice versâ*.

Thus, 0·1 per cent. in the dilution of a blend of 140·4 tons is equivalent to 140·4 × 0·001 ton of water = 0·1404 ton.

Difference in strength of oleum and Grillo sulphuric acid is 105·0 — 98·6 = 6·4 per cent.

Now, the extra water introduced by replacing 1 ton of oleum by 1 ton of Grillo sulphuric acid is 0·064 ton, and 0·1 per cent. in dilution is equivalent to 0·1464 tons H_2O.

∴ A dilution error of 0·1 per cent. is counteracted by the addition or subtraction of $\frac{0{\cdot}1404}{0{\cdot}0640} = 2{\cdot}2$ tons of oleum.

∴ For every 0·1 per cent. of dilution in excess of 2·7 per cent., an additional 2·2 tons of oleum must be added to subsequent blends, and for every 0·1 per cent. of dilution below 2·7 per cent. each blend requires 2·2 tons less of oleum.

The necessary compensation to be made in the amount of Grillo sulphuric acid is made when the latter is added to the mixes in the blender when the final dip is being made up to 9 feet.

MNT Mixed Acid.—The preparation of MNT mixed acid is governed by the following facts:—

(1) MNT and TNT mixed acids must respectively be produced in the proportions required for the two stages of the nitration process, viz., mono- and trinitration.

(2) The whole of the weak nitric acid (50 per cent.) produced at the denitrators and retort absorption towers must be incorporated at once in MNT mixed acid (*see* page 35).

It is important to avoid the opposite dangers of over- and under-production. Of these the first is the greater and the more difficult to control if production gets out of hand. It has proved most desirable in routine practice to under-produce MNT mixed acid.

At the plant efficiencies obtaining at the beginning of the year 1917, for every 100 tons of TNT produced, 31·1 tons of HNO_3 are required for the necessary MNT mixed acid. Of this amount, 18·9 tons of HNO_3 are received from the denitrators and 3·3 tons of HNO_3 from the absorbers at the retort house, leaving 8·9 tons of HNO_3 to be provided out of the retort production of strong nitric acid (88 per cent).

Sulphuric acid of 97 per cent. strength is required to mix with this nitric acid in order to yield MNT mixed acid of the required specification. By making the standard MNT mixes with the Grillo 98·6 per cent. sulphuric acid, less strong nitric acid is used than is actually required, and the MNT mixed acid is therefore slightly under-produced. This is compensated for by making mixes, at intervals of a week or so, with concentrated sulphuric acid from the Gaillard towers of 90 per cent. or 91 per cent. Such mixes utilise more strong nitric acid than is required by the acids balance.

MNT mixed acid is not made in blends, but in mixes, the number of mixes in each blend depending upon convenience in doping; usually 5–7 mixes constitute one blend. The determining factor in calculating each mix is that the charge of 34½ inches, *i.e.*, 11·17 tons, of sulphuric acid of either 98·6 per cent. or 90 per cent. is first run down into the mixer, and the amount of nitric acid necessary to give the correct analysis is calculated and added. Mixes are calculated to give an analysis of H_2SO_4 59·5, HNO_3 22·5, H_2O 18·0, which can afterwards be doped with a 97 per cent. sulphuric acid.

The mix with Grillo 98·6 per cent. sulphuric acid works out as follows:—

11·17 tons of 98·6 per cent. sulphuric acid.
1·27 tons of 89 per cent. nitric acid.
6·06 tons of 50 per cent. nitric acid.

Total - - - 18·50 tons.

As this quantity exceeds the capacity of the mixer, four or five inches are pumped away (after cooling) before the last ton of nitric acid is added.

The mix with Gaillard 90 per cent. sulphuric acid works out to be:—

11·17 tons of 90 per cent. sulphuric acid.
2·39 „ „ 89 „ „ nitric acid.
3·34 „ „ 50 „ „ „ „

Total - 16·90 tons.

For practical purposes, both mixes are set out in tabular form in order that adjustments may be made for nitric acid from the retort absorption towers of strengths exceeding 50 per cent.

The rate of making mixes is determined by the rate at which the denitrator and retort absorption towers produce weak nitric acid. A standing rule in mixing is that such acid must be mixed off as soon as possible. This is important for the following reasons:—

(1) Limited storage capacity for weak nitric acid from the denitrator plant.

(2) The necessity for maintaining a sufficient proportion of the storage capacity for weak nitric acid from the retorts for use in the event of a strong nitric acid cooling coil developing a leak. In this case it would be necessary to run strong nitric acid as quickly as possible into the so-called weak acid receiver.

The necessity for making mixes with Gaillard sulphuric acid of 90 per cent. strength, and the number of such mixes to be made are judged by keeping a record (similar to that given below) of the make of TNT and MNT mixed acids.

Week ending October 13th, 1917.

Date: 24 hours ending October.	TNT mixed acid produced.	Equivalent amount of MNT mixed acid	Actual amount of MNT mixed acid produced	Excess of MNT mixed acid produced.	Total to date.
	Tons.	Tons.	Tons.	Tons.	Tons.
7	161·7	49·6	54·6	+ 5·0	5·0
8	163·8	50·2	97·6	+ 47·4	52·4
9	461·2	141·4	120·2	— 21·2	31·2
10	325·2	99·7	118·5	+ 18·8	50·0
11	511·6	156·9	131·6	- 25·3	24·7
12	467·9	143·5	148·1	+ 4·6	29·3
13	481·3	147·6	131·3	— 16·3	13·0

The equivalent amount of MNT mixed acid is equal to $\frac{\text{Amount of TNT mixed acid produced} \times 1{\cdot}47}{4{\cdot}78}$, where 1 ton of TNT requires 4·78 tons of TNT mixed acid and 1·47 tons of MNT mixed acid.

These records are kept in graphical form as shown in Fig. 12.

Whenever the tonnage of MNT mixed acid falls seriously below the amount required to keep pace with the production of TNT mixed acid, the mix with Gaillard sulphuric acid is resorted to until the deficiency has been made good.

Advantages of the procedure adopted.—It will be seen that for both TNT and MNT mixed acids a standard charge of 34½ inches of Grillo 98·6 per cent. sulphuric acid is added. As a general rule, unless instructions are given to the contrary, no mixer is ever left empty, and persons in charge of the plant are given instructions to run down 34½ inches of Grillo sulphuric acid as a matter of routine as soon as every mix has been pumped away. The advantages of this procedure are as follows:—

(*a*) The charge can be used either for a TNT or an MNT mix, as occasion demands.

(*b*) As routine prescribes the same sulphuric acid charge in all cases (except under explicit and somewhat exceptional instructions to the contrary), there is less liability to error through the addition of nitric acid to the wrong sulphuric acid charge for any mix.

(*c*) Awkward situations are avoided which might otherwise arise through nitric acid, oleum, or water from a leaking coil escaping into a mixer and causing trouble on account of the acid contained therein being below the mixing level. If anything does leak into the mixer it is at once mixed into the bulk of the acid.

(*d*) By allowing the charge of sulphuric acid to stand for a while before nitric acid is run in, leakages from valves or coils can readily be detected by a rise in either the temperature or the acid level.

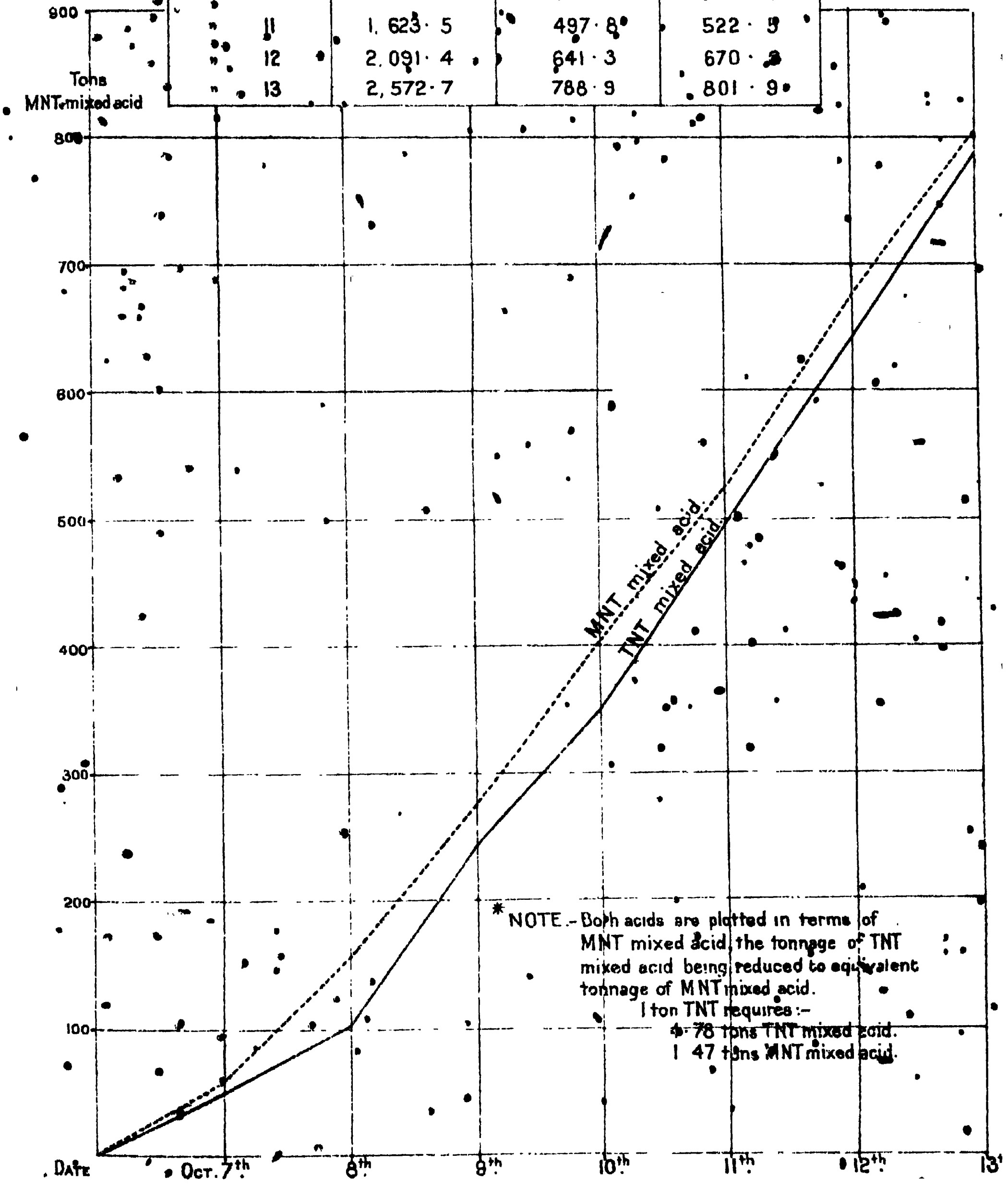
THE CALCULATION OF DOPES.

Possible Dopes.—If a blend is found on analysis to be incorrect, four kinds of dope are theoretically possible for its adjustment:—

(a) *A nitric acid dope*, when the H_2SO_4 content is high. In this case the tonnage of the dope adjusts the H_2SO_4 content of the blend, whilst the strength of the nitric acid used corrects the HNO_3 content and the dilution.

GRAPH TO SHOW COMPARATIVE PRODUCTIONS OF TNT AND MNT MIXED ACIDS.

From 6 a.m. on Oct 6th to 6 a.m. on.	TOTAL PRODUCTIONS FOR WEEK TO DATE.		
	Tonnage of TNT Mixed Acid.	Equivalent Tonnage of MNT Mixed Acid.*	Actual Tonnage of MNT Mixed Acid.
Oct. 7	161·7	49·6	54·6
" 8	325·5	99·8	152·2
" 9	786·7	241·2	272·4
" 10	1,111·9	340·9	390·9
" 11	1,623·5	497·8	522·9
" 12	2,091·4	641·3	670·3
" 13	2,572·7	788·9	801·9



*NOTE.- Both acids are plotted in terms of MNT mixed acid, the tonnage of TNT mixed acid being reduced to equivalent tonnage of MNT mixed acid.
1 ton TNT requires:-
4·78 tons TNT mixed acid.
1 47 tons MNT mixed acid.

FIG. 12.

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(b) *A sulphuric acid dope*, when the HNO_3 content is high. This is analogous to (a). The tonnage corrects the HNO_3, whilst the strength is chosen so as to adjust the H_2SO_4 content and the dilution.

(c) *A water dope.*—This has never been employed in TNT acid mixing. The dope is useful, however, when mixing within narrow limits, to increase the dilution when this is low, and the HNO_3 correct or slightly high, and the H_2SO_4 is 0·1 or 0·2 per cent. above the specified figure.

(d) *A mixed sulphuric and nitric acid dope*, which corrects a blend in which neither the HNO_3 nor the H_2SO_4 content is sufficiently high to allow of a sulphuric or nitric acid dope with the acids available.

The two principal methods used are (b) and (d).

Practical Methods of Doping.—It is obviously desirable that some scheme should be drawn up whereby the operation of doping is sufficiently simplified to permit of foremen dealing with all dopes which cannot be termed exceptional. The first step in this direction resulted in the drawing up of forms for doping, which covered the cases of dopes (b) and (d), specimens of which are given later. It was necessary to provide in addition, however, some kind of check to calculation in order to give confidence and to guard against error. This information was first presented in the form of graphs, but experience showed that the reduction of the graphs to tabular form gave the results in a clearer and more permanent form. Tables were then constructed to deal with all the principal dopes, which resulted in calculations being reduced to a minimum.

The tables constructed do not aim at giving a dope for every possible contingency; that would be manifestly impossible, and in any case the tables would be too long and cumbersome for the purpose required. It proved possible, however, to construct a series of simple tables which when combined would deal with almost an infinite variety of incorrect blends.

Dopes for TNT Mixed Acid—(a) **Sulphuric Acid Dope.**—Three tables are required, one to give the tonnage and two to give the percentage of H_2SO_4 in the sulphuric acid required. Required composition:—H_2SO_4 79·5 per cent., HNO_3 17·8 per cent., H_2O 2·7 per cent.

Table 1: *Tonnage of Dope.*—It is sufficient to consider and correct two of the constituents, say, the HNO_3 and the dilution; the H_2SO_4 will be correct by difference. The HNO_3 content and dilution of a blend capable of being doped with sulphuric acid alone will in general terms be respectively:—

$$17{\cdot}8 + n \text{ and } 2{\cdot}7 + d,$$

n being the excess of HNO_3 and d the error in dilution.

The tonnage of the sulphuric acid dope is then equal to—

$$\frac{\text{Tonnage of blend} \times n}{17\cdot8}$$

which is proportional to n. The standard dip of a TNT mixed acid blend is 9 feet, equivalent to 144·4 tons and a table is constructed giving the dope for each 0·1 per cent. by which the HNO_3 exceeds 17·8 per cent. In order to deal with cases in which the dip of the blender exceeds or falls short of 9 feet, the dope for 1 foot (equivalent to 16 tons) is given side by side with that for 9 feet.

Only one main calculation is necessary in constructing the table, viz. :—

The dope for an HNO_3 figure of 18·8 (*i.e.*, where $n = 1\cdot0$)

$$= \frac{144\cdot4 \times 1\cdot0}{17\cdot8} = 8\cdot11 \text{ tons.}$$

∴ Dope for 0·1 per cent. excess HNO_3 = 0·811 tons.

" " 0·2 " " " " = 1·622 tons, and so on.

∴ Dope for 1 per cent. excess of HNO_3 per 1 foot of the blend $= \frac{8\cdot11}{9} = 0\cdot90$ tons.

TABLE I.

Tonnage of Dope.

HNO_3 content of blend.	Dope for 9 feet.	Correction for 1 foot	HNO_3 content of blend	Dope for 9 feet	Correction for 1 foot.
17·8	Nil	Nil	19·3	12·17	1·35
17·9	0·81	0·09	19·4	12·98	1·44
18·0	1·62	0·18	19·5	13·79	1·53
18·1	2·43	0·27	19·6	14·60	1·62
18·2	3·24	0·36	19·7	15·41	1·71
18·3	4·06	0·45	19·8	16·22	1·80
18·4	4·87	0·54	19·9	17·03	1·89
18·5	5·68	0·63	20·0	17·84	1·98
18·6	6·49	0·72	20·1	18·65	2·07
18·7	7·30	0·81	20·2	19·46	2·16
18·8	8·11	0·90	20·3	20·28	2·25
18·9	8·92	0·99	20·4	21·09	2·34
19·0	9·73	1·08	20·5	21·90	2·43
19·1	10·54	1·17	20·6	22·71	2·52
19·2	11·35	1·26	20·7	23·52	2·61

Tables 2a and 2b: Percentage of H_2SO_4 in Sulphuric Acid required for Dope.—Assuming as before that the HNO_3 content is $17\cdot8 + n$, and the dilution $2\cdot7 + d$, then in the case of a dilution of $2\cdot7 + d$, for example, the dilution of the dope must be—

$$\left(2\cdot7 - \frac{d \times \text{blend}}{\text{dope}}\right) = \left(2\cdot7 - \frac{d \times 17\cdot8}{n}\right),$$

since the fraction $\frac{17\cdot 8}{n}$, *i.e.*, $\frac{\text{required HNO}_3}{\text{excess HNO}_3}$, and $\frac{\text{blend}}{\text{dope}}$ are equivalent.

$$\therefore \text{Percentage of } H_2SO_4 \text{ required} = 100 - \left(2\cdot 7 + \frac{17\cdot 8 \times d}{n}\right)$$

This figure may exceed 100 per cent., in which case oleum will be required.

The percentage of H_2SO_4 thus varies directly as $\frac{d}{n}$, and can be plotted on a graph against this ratio. It is more convenient, however, to plot it against $\frac{n}{d}$, and from the graph so obtained the percentage of H_2SO_4 for intermediate values of $\frac{d}{n}$ may be read off and tabulated as follows:

TABLE 2A.

Percentage of H_2SO_4 in Sulphuric Acid required by dope.

(Case when dilution is greater than 2·7 per cent.)

$\frac{n}{d}$	Percentage of H_2SO_4 required.	$\frac{n}{d}$	Percentage of H_2SO_4 required.	$\frac{n}{d}$	Percentage of H_2SO_4 required.
1·5	109·2	2·9	103·4	5·6	100·5
1·6	108·5	3·0	103·2	5·8	100·4
1·7	107·8	3·2	102·9	6·0	100·3
1·8	107·2	3·4	102·6	7·0	99·8
1·9	106·7	3·6	102·4	8·0	99·6
2·0	106·2	3·8	102·2	9·0	99·3
2·1	105·7	4·0	102·0	10·0	99·1
2·2	105·3	4·2	101·8	12·0	98·8
2·3	105·0	4·4	101·6	14·0	98·6
2·4	104·7	4·6	101·4	16·0	98·4
2·5	104·4	4·8	101·2	18·0	98·3
2·6	104·1	5·0	101·0	20·0	98·2
2·7	103·9	5·2	100·8	30·0	97·9
2·8	103·6	5·4	100·7	40·0	97·7

n = excess of HNO_3 in blend; d = error in dilution.

(N.B.—When the ratio $\frac{n}{d}$ is less than 1·5, it is not possible to dope with sulphuric acid alone.)

If the dilution is 2·7 − d, the percentage of H_2SO_4 in the dope must then be $100 - \left(2\cdot 7 + \frac{17\cdot 8 \times d}{n}\right)$, and the second graph and table have been drawn up on similar lines to meet this case.

TABLE 2B.

Percentage of H_2SO_4 in Sulphuric Acid required by Dope.

(Case when dilution is less than 2·7 per cent.)

$\frac{n}{d}$	Percentage of H_2SO_4 required.	$\frac{n}{d}$	Percentage of H_2SO_4 required.	$\frac{n}{d}$	Percentage of H_2SO_4 required.
1·1	81·1	3·0	91·4	5·8	94·2
1·2	82·2	3·2	91·7	6·0	94·3
1·3	83·3	3·4	91·9	6·5	94·5
1·4	84·4	3·6	92·1	7·0	94·8
1·5	85·4	3·8	92·3	8·0	95·1
1·6	86·1	4·0	92·5	9·0	95·3
1·7	86·8	4·2	92·8	10·0	95·5
1·8	87·4	4·4	93·0	12·0	95·8
1·9	87·9	4·6	93·2	14·0	96·0
2·0	88·3	4·8	93·4	16·0	96·2
2·2	89·2	5·0	93·6	18·0	96·3
2·4	89·8	5·2	93·8	20·0	96·4
2·6	90·4	5·4	93·9	30·0	96·7
2·8	91·0	5·6	94·1	40·0	96·9

n = excess of HNO_3 in blend; d = error in dilution.

(N.B.—When the ratio $\frac{n}{d}$ is less than 1·1, it is not possible to dope with sulphuric acid alone.)

The only excluded case is when the dilution is 2·7 per cent., *i.e.*, when it is correct, the percentage of H_2SO_4 then required being 97·3 per cent.

It will be seen that Table 1 gives the tonnage of the dope, given the HNO_3 content and dip of the blend, and that Tables 2A and 2B give the strength of sulphuric acid required, according as the dilution is greater or less than 2·7 per cent. It remains necessary, therefore, only to determine the ratio $\frac{n}{d}$, and, given the quantity and strength of the sulphuric acid required for the dope, the calculation of the amounts of the sulphuric acids which must be used to give a sulphuric acid of the required strength is a simple matter. These amounts can be checked by means of simple straight line graphs.

Assuming that sulphuric acid of the following strengths is available:—

	Per cent.
Oleum - - - - - - - - - -	105·0
Grillo sulphuric acid - - - - - - -	98·6
Gaillard sulphuric acid - - - - - -	91·0
TNT spend acid - - - - - - - -	71·0

three graphs will be required, viz., for sulphuric acid of strengths between—

(1) 71·0 per cent. and 91·0 per cent.
(2) 91·0 ,, ,, 98·6 ,,
(3) 98·6 ,, ,, 105·0 ,,

GRAPH GIVING TONNAGE OF OLEUM (105% H_2SO_4) AND GRILLO SULPHURIC ACID (98·6% H_2SO_4) REQUIRED TO GIVE ANY WEIGHT OF SULPHURIC ACID OF STRENGTH BETWEEN 98·6% AND 105%.

EXAMPLE :- *Required 17·8 tons of Oleum of 101·0% Strength*:-
Tonnage of Oleum = 6·6 tons.
Tonnage of 98·6%.
Sulphuric Acid = 17·8 − 6·6 = 11·2 tons.

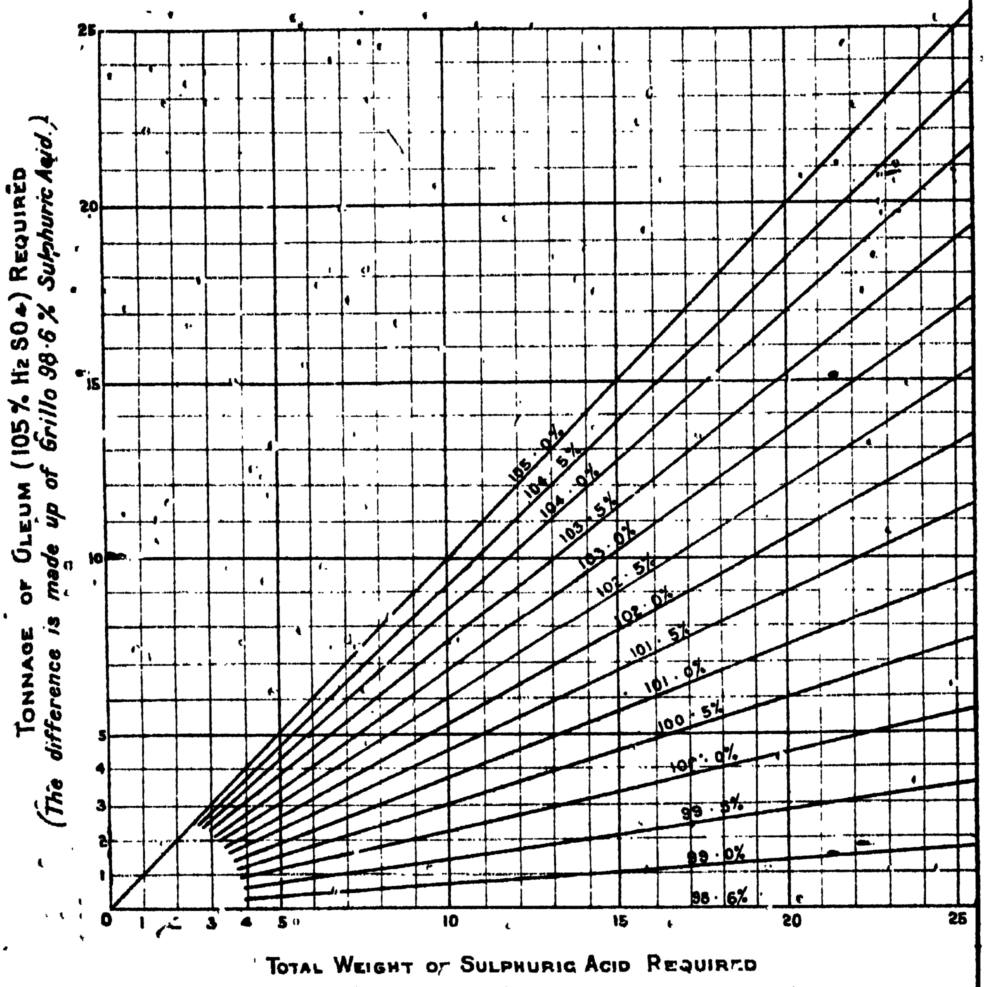

FIG. 13.

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Consideration of the last of these will indicate the general method of procedure adopted.

	Per cent.	
Strength of oleum - - - -	105·0	
" " sulphuric acid required -	98·6 + d	difference
" " Grillo sulphuric acid - -	98·6	= d per cent.

Total difference between the percentages of H_2SO_4 in the oleum and in the Grillo sulphuric acid = 6·4 per cent.

∴ Amount of oleum in w tons of sulphuric acid at $(98 \cdot 6 + d)$ per cent. $= \frac{w \times d}{6 \cdot 4}$ *i.e.*, the tonnage of oleum is directly proportional both to the total tonnage of the mixed sulphuric acid required for the dope and to the difference d between the strength of that sulphuric acid and the strength of the Grillo sulphuric acid.

It is found convenient to draw up a series of straight line graph for strengths of sulphuric acid varying in 0·5 per cent. steps fror 98·6 per cent. up to 105 per cent. The most suitable point to determin on each line is found by taking a total tonnage of a suitable multipl of the difference in H_2SO_4 content between oleum and Grillo sulphuri acid, viz., 6·4 per cent. Such a multiple would be 6·4 × 4 = 25·6 ton and for every additional 0·5 per cent. difference the tonnage of oleur will be increased by 2·0.

Fig. 13 illustrates this point, and shows the graph for sulphuri acid of strengths from 98·6 per cent. to 105 per cent. This type graph possesses the advantage that on account of its simplicity it ca be readily redrawn if any changes in the strengths of the available sulphuric acid necessitate that this should be done.

TABLE 3.

Percentage of H_2SO_4 in sulphuric acid required.	Difference in H_2SO_4 content between the sulphuric acid required and Grillo sulphuric acid (98·6 per cent.)	Tonnage of oleum in 25·6 tons of sulphuric acid of the required strength.
99·0	0·4	1·6
99·5	0·9	3·6
100·0	1·4	5·6

Dopes for TNT Mixed Acid—(b) Mixed Acid Dope.—This dope is not often necessary, but it is occasionally desirable in the following cases:—

(*a*) If insufficient nitric acid has been added to the preliminary mixes.

(*b*) If an excess of Grillo 98·6 per cent. sulphuric acid has been run into the blender, causing the dip to exceed 9 feet, and thereby lowering the percentage of HNO_3 in the blend.

(c) When the dilution error is considerable, causing the ratio $\frac{n}{d}$ to be very low, thus making a sulphuric acid dope impossible.

Under any one of these circumstances, three courses are open :—

(1) The HNO_3 content of the blend can be increased by adding strong nitric acid to a charge of 34½ inches which has been pumped back from the blender to a mixer (a pumping line connecting the sludge exits of the blenders to the mixers exists for this purpose). Sufficient nitric acid can then easily be added to give an HNO_3 content in the blend which is high enough to allow of a sulphuric acid dope being made in the usual manner.

(2) If the HNO_3 content is lower than that required by specification, a dope of nitric acid is possible in certain cases, provided the required strength is between 50 per cent. and 90 per cent. This is added as in (1) to a portion of the blend pumped back to the mixer.

(3) A dope of mixed sulphuric and nitric acids can be made. The mixed acid dope is usually resorted to in the case of TNT mixed acid. Methods (1) and (2) are occasionally useful, however, particularly as regards MNT mixed acid; these cases will be considered later.

In order to reduce the mixed acid dope to tabular form, it is necessary for the tonnage of the blend to be constant. This is not a practical difficulty, for the standard dip of blends of TNT mixed acid is 9 feet, and in any case the occasional errors are on the high side. It is therefore an easy matter before doping to reduce the level of the blend when necessary to 9 feet by levelling down to the next blender.

Three tables are in use, two of which may suffice. The first tables give the dopes for standard blends of varying HNO_3 content but with correct dilutions. Given these, it is a simple matter to introduce corrections for the errors in dilution.

Table 4: Dope for varying HNO_3 content but correct Dilution.—The calculations for this table are quite simple if the case be first considered of the dope for a blend containing 17·8 per cent. of HNO_3. The dope in the latter case will of course be of correct analysis, viz., H_2SO_4 79·5 per cent., HNO_3 17·8 per cent., H_2O 2·7 per cent. Assuming the dope to consist of 17 tons, then it contains 17 × 0·178 = 3·03 tons of HNO_3, and 17 × 0·795 = 13·52 tons of H_2SO_4. Given a nitric acid of any fixed strength (here taken as 86 per cent.) the tonnage of the nitric acid and the tonnage and strength of the sulphuric acid naturally follow. The rest of the table is based on the fact that 0·1 per cent. in acidity is equivalent to 1·444* × 0·1 = 0·1444 ton of acid, *i.e.*, if the HNO_3 content is 17·7 per cent. the tonnage of HNO_3 required for the dope is equal to the tonnage of HNO_3 required for doping a blend containing 17·8 per cent. of HNO_3 less 0·1444 ton, and the tonnage of H_2SO_4 in the dope will therefore be equal to the tonnage of H_2SO_4 required for doping a blend containing 17·8 per cent. of HNO_3 plus 0·1444 ton. This

follows from the fact that the dilution, and hence the total acidity, in all the dopes in this table must be constant.

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* *See* page 48.

A table is first drawn up in the following form:—

HNO_3 content.	Nitric acid.	HNO_3	H_2SO_4	Sulphuric acid.	H_2SO_4 in sulphuric acid.	Oleum
Per cent. *a*	Tons. *b*	Tons. *c*	Tons. *d*	Tons. *e*	Per cent. *f*	Tons. *g*

c and *d* are calculated, as indicated above, for the various HNO_3 contents which it is desired to dope. This having been done, *b* is readily obtainable from the tonnage of HNO_3 required and the most general strength available; $e = 17 - b$; $f = \frac{d \times 100}{e}$; and finally $g = \frac{f \times (f - 98{\cdot}6)}{6{\cdot}4}$, when the oleum available is of 105 per cent. H_2SO_4, and the Grillo sulphuric acid of 98·6 per cent. H_2SO_4.

In presenting the table for practical use only the columns giving *a*, *b*, *e*, and *f* are necessary.

The dilution of the blend is corrected by either (*a*) increasing the amount of oleum in the dope, whilst keeping the total tonnage of sulphuric acid constant, in cases where the dilution exceeds 2·7 per cent., or (*b*) decreasing the amount of oleum or including a certain amount of weak sulphuric acid in the dope in cases where the dilution is less than 2·7 per cent.

TABLE 4.

HNO_3 content.	Nitric acid (86 per cent.).	Total sulphuric acid.	Oleum (105 per cent. H_2SO_4).	HNO_3 content.	Nitric acid (86 per cent.).	Total sulphuric acid.	Oleum (105 per cent. H_2SO_4).
Per cent.	Tons.	Tons.	Tons.	Per cent.	Tons.	Tons.	Tons.
16·0	6·5	10·5	9·6	17·5	4·0	13·0	4·7
16·1	6·4	10·6	9·2	17·6	3·9	13·1	4·3
16·2	6·2	10·8	8·8	17·7	3·7	13·3	3·9
16·3	6·0	11·0	8·5	17·8	3·5	13·5	3·7
16·4	5·9	11·1	8·0	17·9	3·4	13·6	3·3
16·5	5·7	11·3	7·8	18·0	3·2	13·8	3·0
16·6	5·5	11·5	7·5	18·1	3·0	14·0	2·8
16·7	5·4	11·6	7·2	18·2	2·8	14·2	2·2
16·8	5·2	11·8	6·9	18·3	2·7	14·3	2·0
16·9	5·0	12·0	6·6	18·4	2·5	14·5	1·5
17·0	4·9	12·1	6·2	18·5	2·3	14·7	1·1
17·1	4·7	12·3	5·9	18·6	2·2	14·8	0·9
17·2	4·5	12·5	5·6	18·7	2·0	15·0	0·6
17·3	4·4	12·6	5·2	18·8	1·8	15·0	0·4
17·4	4·2	12·8	4·9				

N.B.—The difference between the total tonnage of sulphuric acid and the tonnage of oleum is to consist of Grillo 98·6 per cent. sulphuric acid.

Table 5: *Correction when dilution exceeds* 2·7 *per cent.*—Taking case (*a*) first, the replacement in the sulphuric acid of the dope of 1 ton of Grillo 98·6 per cent. sulphuric acid by 1 ton of oleum (105 per cent. H_2SO_4) is equivalent to reducing the tonnage of water in the dope, and therefore in the final blend, by 0·064 ton.

∴ 0·1 per cent. dilution in a blend of 144·4 tons is equivalent to 0·1444 ton.

∴ Tonnage of oleum required to replace Grillo 98·6 per cent. acid in compensating for a dilution 0·1 per cent. too high is—

$$\frac{0\cdot1444}{0\cdot064} = 2\cdot22 \text{ tons.}$$

Table 5 shows this in tabular form, giving the tonnage of oleum equivalent to a given error in dilution.

TABLE 5.

Error in dilution.	Equivalent of oleum.	Error in dilution.	Equivalent of oleum.
Per cent.	Tons.	Per cent.	Tons.
0·1	2·2	0·6	13·3
0·2	4·4	0·7	15·5
0·3	6·7	0·8	17·8
0·4	8·9	0·9	20·0
0·5	11·1	1·0	22·2

In order to illustrate the use of the two tables, the instance may be taken of a blend containing H_2SO_4 80·0 per cent., HNO_3 17·1 per cent., and H_2O 2·9 per cent.

Table 4 gives the dope for a blend containing 17·1 per cent. of HNO_3 and of correct dilution as—

4·7 tons of 86 per cent. nitric acid;
12·3 tons of sulphuric acid (total); and
5·9 tons of oleum (105 per cent. H_2SO_4).

The dilution is 0·2 per cent. higher than 2·7 per cent., and Table 5 shows this to be equivalent to 4·4 tons of oleum.

∴ Total oleum in dope is (5·9 + 4·4) = 10·3 tons, and the tonnage of Grillo 98·6 sulphuric acid by difference is (12·3 — 10·3) = 2·0 tons.

The dope should therefore consist of
10·3 tons of oleum (105 per cent. H_2SO_4).
2·0 tons of Grillo sulphuric acid (98·6 per cent. H_2SO_4).
4·7 tons of nitric acid (86·0 per cent. HNO_3).

Table 6: *Correction when the dilution is less than* 2·7 *per cent.*—If the case of a blend of analysis H_2SO_4 80·6 per cent., HNO_3 17·1 per cent., and H_2O 2·3 per cent. be now considered, the dope for correct dilution is the same as in the previous case. The dilution is 0·4 per cent. lower than 2·7 per cent., however, and it will in this case be necessary to replace oleum by Grillo 98·6 per cent. sulphuric acid. The tonnage of oleum equivalent to an error in dilution of 0·4 per cent. is given in Table 5 as 8·9 tons, and the tonnage of oleum in the dope should therefore be (5·9 − 8·9) = − 3·0 tons. The meaning of this is that the replacement of all the oleum by Grillo 98·6 sulphuric acid (viz., 5·9 tons) would still be insufficient to supply the water necessary to dilute the blend to 2·7 per cent.

In actual practice it is customary to replace a certain amount of the Grillo 98·6 per cent. acid by Gaillard concentrated acid of 91 per cent.

Oleum contains - 105·0 per cent. H_2SO_4 } Difference = 6·4
Grillo acid contains - 98·6 " " } per cent.
Gaillard concentrated acid contains - 91·0 per cent. H_2SO_4 } Difference = 7·6 per cent.

If these two differences were equal, then the − 3·0 tons of oleum in the above calculation would signify that 3 tons of Gaillard 91 per cent. acid would be required in the dope.

With the differences as they are, however, 1·0 ton of oleum is equivalent to $\frac{6{\cdot}4}{7{\cdot}6} = 0{\cdot}84$ tons of 91·0 per cent. sulphuric acid, the reason being that the figure − 3·0 tons of oleum obtained above requires, in addition to the replacement of all the oleum by 98·6 per cent. sulphuric acid, a further quantity of water in order to increase the dilution of the blend. This quantity is equal to the water content of 3 tons of 98·6 per cent. sulphuric acid less the water content of 3 tons of oleum, *i.e.*, 3 × 0·064 ton. Now the replacement of 1 ton of 98·6 per cent. sulphuric acid by 1 ton of 91·0 per cent. acid increases the water in the dope by 0·076 ton. The tonnage of 91·0 per cent. acid which is equivalent to − 3·0 tons of oleum is therefore

$$\frac{3 \times 0{\cdot}064}{0{\cdot}076} = 3 \times 0{\cdot}84 \text{ tons.}$$

Table 6 is as follows, and is used when the tonnage of oleum as calculated is a negative quantity in order to convert − x tons of oleum into equivalent tons of sulphuric acid of 91 per cent. strength.

TABLE 6.

Oleum.	91 per cent. sulphuric acid.	Oleum.	91 per cent sulphuric acid.
Tons.	Tons.	Tons.	Tons.
−1·0	0·84	−20·0	16·80
−2·0	1·68	−0·1	0·08
−3·0	2·52	−0·2	0·16
−4·0	3·36	−0·3	0·25
−5·0	4·20	−0·4	0·34
−6·0	5·04	−0·5	0·42
−7·0	5·88	−0·6	0·50
−8·0	6·72	−0·7	0·59
−9·0	7·56	−0·8	0·67
−10·0	8·40	−0·9	0·76

One more example is given, in order to illustrate the use of the foregoing tables, viz., that of a blend containing H_2SO_4 80·4 per cent., HNO_3 17·3 per cent., H_2O 2·3 per cent. :—

(*a*) From Table 4 the dope for correct dilution but incorrect HNO_3 content is given as—

Nitric acid (86 per cent. HNO_3)	4·4 tons.
Total sulphuric acid	12·6 „
Oleum (105 per cent. H_2SO_4)	5·2 „

(*b*) The dilution error is (2·7 – 2·3) = 0·4 per cent., and from Table 5 the quantity of oleum equivalent to this is 8·9 tons.

∴ Quantity of oleum in dope is (5·2 – 8·9) = – 3·7 tons.

(*c*) From Table 6 it will be seen that – 3·7 tons of oleum are equivalent to (2·52 + 0·59) = 3·1 tons of 91 per cent. sulphuric acid.

The remainder of the sulphuric acid is to be made up with Grillo 98·6 per cent. acid.

∴ Quantity of 98·6 per cent. sulphuric acid required is (12·6 – 3·1) = 9·5 tons.

The dope required will therefore consist of :—

Nitric acid (86 per cent.)	4·4 tons.
Sulphuric acid (98·6 per cent.)	9·5 „
Sulphuric acid (91 per cent.)	3·1 „

Dopes for TNT Mixed Acid—(c) Exceptional cases. It may happen that the 17-ton dope referred to on page 52 and subsequently is not large enough to effect the necessary correction in the blend. Such a case will be indicated by the calculated quantity of oleum or 91 per cent. sulphuric acid required being greater than the total tonnage of sulphuric acid in the dope, and this necessitates a fresh starting point.

For instance, a 34-ton dope, *i.e.*, a double dope, would be necessary with a blend of analysis H_2SO_4 79·6 per cent., HNO_3 17 per cent., H_2O 3·4 per cent. A 17-ton dope for a blend of correct dilution but which contains 17 per cent. of HNO_3 is given in Table 4. If a 34-ton dope is required the extra 17-ton dope must be correct as regards HNO_3 content, since the first dope is sufficient to correct the blend in respect of this constituent.

The 17-ton dope for HNO_3 = 17 per cent. contains (*see* Table 4) :—

Nitric acid (86 per cent. HNO_3)	4·9 tons.
Total sulphuric acid	12·1 „
Oleum (105 per cent. H_2SO_4)	6·2 „

The extra 17 tons for HNO_3 = 17·8 per cent. contains (*see* Table 4) :—

Nitric acid (86 per cent. H_2SO_4)	3·5 tons.
Total sulphuric acid	13·5 „
Oleum (105 per cent. H_2SO_4)	3·7 „

The 34-ton dope for HNO_3 = 17 per cent. contains :—

Nitric acid (86 per cent. HNO_3)	8·4 tons.
Total sulphuric acid	25·6 „
Oleum (105 per cent. H_2SO_4)	9·9 „

The error in dilution is (3·4 – 2·7 = 0·7 per cent.).

Extra oleum required (*see* Table 5) = 15·5 tons, and the total oleum required will therefore be (9·9 + 15·5) = 24·4 tons.

∴ Grillo 98·6 per cent. sulphuric acid required is (25·6 − 24·4) = 1·2 tons.

The actual dope therefore consists of :—

Nitric acid (86 per cent. HNO_3)	10·4 tons.
Sulphuric acid (98·6 per cent. H_2SO_4)	1·2 „
Oleum (105 per cent. H_2SO_4) - -	24·4 „

and this would be divided into two equal mixes.

Hence the rule :- If a larger dope than 17 tons is required, the starting point must be the sum of (*a*) the ordinary 17-ton dope for the actual HNO_3 content of the blend, and (*b*) a fraction or multiple of the 17-ton dope for a blend of correct analysis, *i.e.*, in which the HNO_3 content is 17·8 per cent.

Dopes for MNT Mixed Acid—(a) Sulphuric Acid Dope.—The general dope is of sulphuric acid, and tables have been constructed similar to those used in the case of TNT mixed acid.

Dope for MNT Mixed Acid—(b) Nitric Acid Dope.—Tables have also been constructed for the use of a nitric acid dope in cases in which the HNO_3 content is low. These are constructed on similar lines to the sulphuric acid dope tables, and are set out as indicated below.

Specification Limits for MNT Mixed Acid.

	Per cent.
H_2SO_4 - - - - - - - - -	62·0
HNO_3 - - - - - - -	21·0
H_2O - - - - - - - - -	17·0
	100·0

The tonnage of nitric acid required for a blend of 8 feet dip is 119·3 tons.

TABLE 7.

Correction for Low HNO_3 Content.

H_2SO_4 in original blend	Nitric acid required.	Correction for each 1 foot dip.	H_2SO_4 in original blend.	Nitric acid required	Correction for each 1 foot dip.
%	Tons.	Tons.	%	Tons.	Tons.
62·0	Nil	Nil	63·1	2·11	0·26
62·1	0·19	0·02	63·2	2·30	0·29
62·2	0·38	0·05	63·3	2·50	0·31
62·3	0·58	0·07	63·4	2·69	0·34
62·4	0·77	0·10	63·5	2·88	0·36
62·5	0·96	0·12	63·6	3·07	0·38
62·6	1·15	0·14	63·7	3·27	0·41
62·7	1·34	0·17	63·8	3·46	0·43
62·8	1·53	0·19	63·9	3·65	0·46
62·9	1·73	0·22	64·0	3·84	0·48
63·0	1·92	0·24			

TABLE 8A.

Percentage of HNO_3 in Nitric Acid required by Dope.

(Case when dilution is less than 17·0 per cent.)

$\frac{s}{d}$	Percentage of HNO_3 required.	$\frac{s}{d}$	Percentage of HNO_3 required.	$\frac{s}{d}$	Percentage of HNO_3 required.
1·0	21·0	2·9	61·6	6·5	73·2
1·5	41·7	3·0	62·3	7·0	74·0
1·6	44·0	3·2	63·5	7·5	74·7
1·7	47·0	3·4	64·6	8·0	75·2
1·8	48·5	3·6	65·6	8·5	75·7
1·9	50·4	3·8	66·6	9·0	76·2
2·0	52·0	4·0	67·5	10·0	76·8
2·1	53·5	4·2	68·3	12·0	77·8
2·2	55·0	4·4	69·0	14·0	78·6
2·3	56·2	4·6	69·7	16·0	79·1
2·4	57·5	4·8	70·2	18·0	79·6
2·5	58·2	5·0	70·6	20·0	80·0
2·6	59·0	5·5	71·7	30·0	80·9
2·7	60·0	6·0	72·5	40·0	81·4
2·8	60·8				

s = excess of H_2SO_4 in blend ; *d* = error in dilution.

TABLE 8B.

Percentage of HNO_3 in Nitric Acid required by Dope.

(Case when dilution is greater than 17·0 per cent.)

$\frac{s}{d}$	Percentage of HNO_3 required.	$\frac{s}{d}$	Percentage of HNO_3 required.	$\frac{s}{d}$	Percentage of HNO_3 required.
4·0	98·5	5·6	94·1	10·0	89·2
4·2	97·6	5·8	93·8	12·0	88·3
4·4	97·0	6·0	93·5	14·0	87·5
4·6	96·3	6·5	92·6	16·0	86·8
4·8	95·8	7·0	91·2	18·0	86·5
5·0	95·3	7·5	91·2	20·0	86·0
5·2	94·9	8·0	90·7	30·0	85·0
5·4	94·5	9·0	90·0	40·0	84·5

s = excess of H_2SO_4 in blend ; *d* = error in dilution.

(N.B.—When the ratio $\frac{s}{d}$ is less than 4·0, it is not possible to dope with nitric acid alone. If the dilution is correct, *i.e.*, 17·0 per cent., the nitric acid required must contain 83 per cent. of HNO_3.)

As explained on page 52, the method of making the dope is to pump 34½ inches of the blend back into the mixer, after which the necessary nitric acid is added. In applying Table 8A, when the dope consists of nitric acid containing less than 80 per cent. of HNO_3, there is a danger of increasing the dilution of the mix above 20 per cent. This is undesirable and in practice care is taken never to exceed a dilution of 20 per cent. in a steel mixer. Some method is necessary, therefore, in order to indicate the amount of nitric acid of a particular strength which can be added to 34½ inches of an MNT blend in a mixer. This is arrived at as follows:—

34½ inches of MNT, mixed acid are equivalent to 10·4 tons. If $(20 - d)$ per cent. represents the actual dilution of the blend to be doped; if the dilution permissible is 20 per cent.; and if $(20 + e)$ per cent. represents the dilution of the nitric acid used in the dope, then the quantity of nitric acid of dilution $(20 + e)$ per cent. which when added to 10·4 tons of MNT mixed acid of dilution $(20 - d)$ per cent. yields a mixture of dilution 20 per cent. is equal to $\frac{10{\cdot}4 \times d}{e}$ tons. This may be either calculated, or given in tabular form against the inverse fraction $\frac{e}{d}$, which is usually greater than unity.

If the dope contains more than this prescribed quantity of nitric acid, then it will be necessary to pump back more than one charge of 34½ inches of the original blend to the mixers.

Dope for MNT Acid.—(c) Mixed Acid Dope.—If neither a nitric acid nor a sulphuric acid dope is possible, then a mixed dope is necessary. This is the only dope which is calculated direct. In this case, also, if the dilution is less than 17·0 per cent., care must be exercised to avoid making a compensating mix having a dilution exceeding 20 per cent.

This is best effected by first calculating the minimum dope possible to correct the blend in order to keep within the 20 per cent. dilution limit.

If,

Dilution of blend - - $(17{\cdot}0 - d)$ per cent.
Required dilution - - - 17·0 per cent. } Difference = 3·0
Maximum dilution of dope = 20·0 „ } per cent.

Then, if the tonnage of the blend is equal to x, the minimum tonnage of the dope (*i.e.*, the tonnage of a dope of 20 per cent. dilution) is equal to $\frac{x \times d}{3{\cdot}0}$.

The dope must not be less than this figure. It is usually greater, in order to make it a multiple of 17 tons, *i.e.*, in order to permit of an exact number of similar mixes being made.

SECTION 3.

PLANT AND PROCESS FOR ACID MIXING.

Whereas Section 1 dealt chiefly with the relation of the work of the mixing plants to the acids cycle as a whole, and Section 2 with the economical utilisation of the available acids, together with the reduction to simple tabular forms of the calculations involved in mixing and doping, this section deals with the plant from the works standpoint.

General. The acid mixing plant consists of the following component parts, viz., storage for mixed and unmixed acids, together with the various pipe-lines for distributing the same; seven preliminary mixing tanks (mixers); four blending tanks (blenders); arrangements for distributing the acid; buildings for enclosing same, &c.

It is more convenient, as a general rule, to treat plant and process together, and this course has been followed in the order of the successive stages of the mixing process.

STORAGE OF UNMIXED ACID AND DELIVERY TO MIXERS.

Storage accommodation.—In discussing storage accommodation for an acid mixing plant it must be realised that the storage capacity needed for nitric acids is totally different from that supplied for sulphuric acids and oleum. For the latter, it is sound policy to carry about two days' stock, with accommodation for three days' supply. This permits mixing to continue during any shut down or temporary shortage of production on the part of the concentration and SO_3 producing plants. At the same time, a little elasticity of working is permitted for the latter plants in the event of the nitric acid production fluctuating upon any account.

This is quite unnecessary, however, as regards storage for nitric acid. The rate of production of mixed acid at the mixers is set by the rate of production of nitric acid at the retorts and denitrators, the nitric acid being mixed off as fast as it is produced. The only storage accommodation which is necessary, therefore, is required in order (1) to allow the nitric acid plants ample surplus receiver room for use while the mixers are drawing from full receivers, and (2) to provide sufficient space to receive the nitric acid during any period during which the mixers are unable to take the acid produced. This may be due either to a temporary stoppage of the mixing due to difficulty in doping blends and pumping them to storage, or to the need for repairing the line delivering the nitric acid to the mixers.

Details of Receiving Tank for strong Nitric Acid.—Fig. 14 gives a good general idea of the lead-receiving tanks used to hold strong nitric acid from the retorts. Each tank has an internal diameter of 8 feet 3 inches

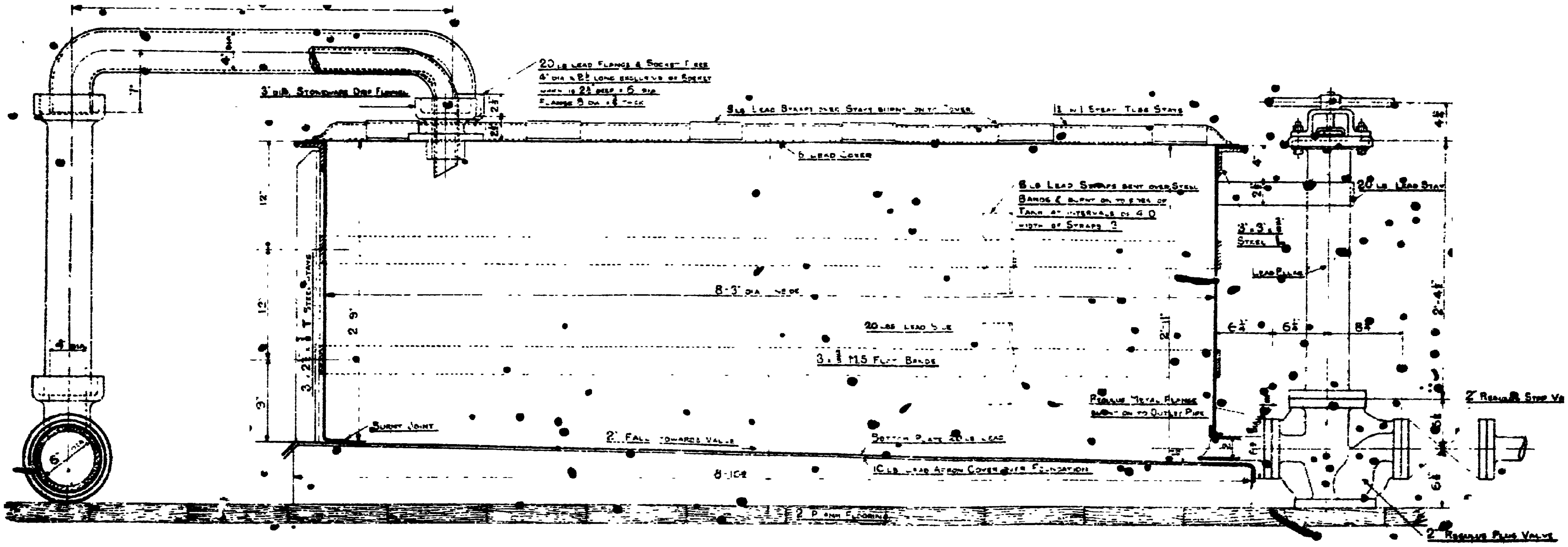

FIG. 14

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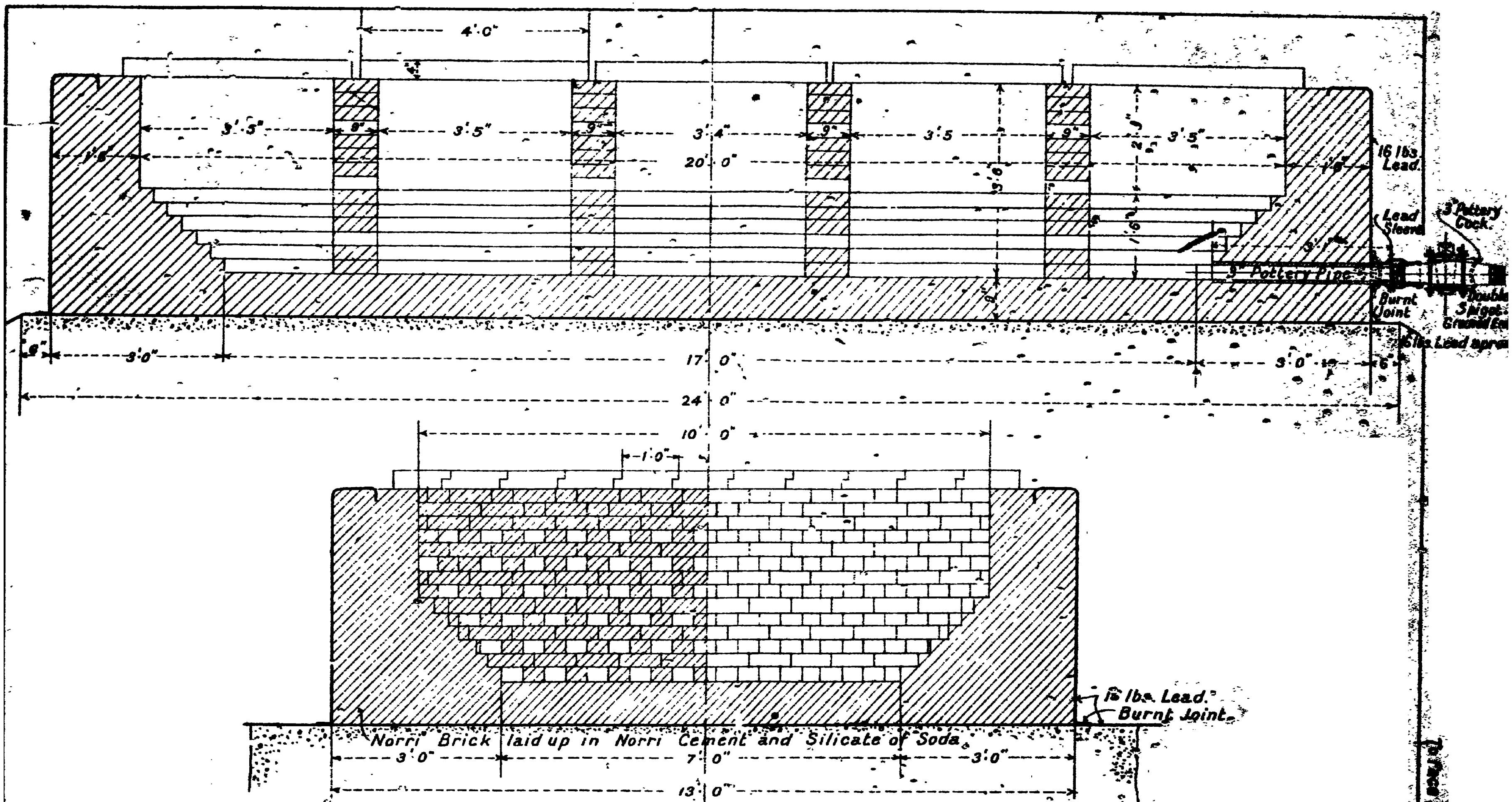

FIG. 15.

with a mean depth of 2 feet 10 inches, a slope being given to the bottom so that the tanks will drain towards the outlet. The lead is carried in a framework consisting of a 3-inch by 3-inch by $\frac{3}{8}$-inch angle ring at the top supported on six 3-inch by $2\frac{1}{2}$-inch by $\frac{3}{8}$-inch tees equally spaced, these tees being further connected together by means of two 3-inch by $\frac{3}{8}$-inch steel bands which serve to prevent the bursting of the lead lining under fluid pressure. The sides and bottom are of 20-lb. sheet lead, the sides being flanged inwards at the bottom and burned inside and outside, and dressed over the top angle as indicated. Care must be taken to round off the corners of the top angle as shown, in order to prevent cutting of the lead. To prevent the lead from "creeping," straps of lead are burned on the sides over the mild steel straps. A cover is provided of 8-lb. lead supported by means of lead straps from $1\frac{1}{2}$-inch diameter pipe bearers. These straps are burned to the cover, and the cover sheet burned round its edge to the side sheets of the tank as detailed.

Before the tank is erected a sheet of 16 lb. lead is laid over the top of the tank foundations, this apron plate being about 6 inches larger in diameter than the foundation block, and being afterwards turned down slightly all round the latter, so that any leakage from the tank will drip clear of the foundations. On this apron plate the bottom sheet of the tank is laid, this being slightly less in diameter than the apron sheet, and this also is turned down at the edges, as shown. The steel framework is then erected, and the side sheets fixed in position.

Acid is introduced into the tank by means of 2-inch lead pipes, which are carried well down inside the tank and burned to the cover. Each tank is provided with gauge glass fittings so that it may be used as a measuring vessel for measuring nitric acid to the mixers. The acid is discharged through a 2-inch diameter opening at the lowest point in the side, this discharge being provided with a 2-inch regulus metal plug-valve. A 4-inch fume pipe is taken from each cover, and the fume pipes from each set of tanks are connected together and led to a battery of condensing towers.

Details of Brick Tank for storing 70 per cent. Nitric Acid. Fig. 15 shows the details of a brick-lined tank as used for the storage of 70 per cent. nitric acid. The tank is built on a concrete foundation on the top of which an apron sheet of 16-lb. lead is laid down upon which the tank is erected. The latter is 20 feet long by 10 feet wide by 3 feet 6 inches deep inside, and is built of acid resisting bricks laid in acid-resisting cement. The bottom of the tank is 9 inches thick, and the sides 18 inches thick at the top and 3 feet 1 inch thick at the bottom, to withstand the static pressure of the acid. Across each tank four 9-inch chequer brick walls are built, these forming supports for the acid-proof tiles forming the cover. These tiles are 4 feet long by 1 foot wide by 4 inches thick, and are formed with rebates so that the joints may be made tight. The outside of the tank is completely covered with 16-lb. sheet lead, the side sheets being brought up over the top and tucked into the brickwork as shown. At the bottom of each tank is provided a 3-inch stoneware outlet, which is fitted with a stoneware cock. This cock is lead covered, the covering being burned to the side sheets of the tank covering, and is further restrained by a lead strap which passes through lugs on the side sheets. In one of the covering tiles a 4-inch hole is cut, and a 4-inch fume pipe inserted therein. It is necessary to exercise particular care in making the joints of this tank, in order that they may be completely acid tight.

Delivery of Acids to Mixers.—The requirements in this respect are best realised by considering what constitutes a complete mixing cycle. This may be said in general terms to comprise the following steps:—

(1) Addition of the sulphuric acid charge.

(2) Addition of the nitric acids and oleum, preliminary mixing and cooling ready for pumping away.

(3) Pumping to bladders.

Steps (1) and (3) constitute the "dead" time for a mix," and are the first points at which speeding up can take place. The pipe-lines delivering the sulphuric acids for the preliminary charge should give as rapid a flow as possible, so as to reduce the time which elapses between the emptying of a mixer and the commencement of the addition of the nitric acid, which may be said to mark the beginning of the actual mix.

The speeds of delivery of acids through the various pipe-lines are given in the following table:—

Acid delivered	Size of pipe-line	Delivery in tons per hour.	Delivery in tons per day.	Hours required per day.
Grillo 98·6 per cent. sulphuric acid	3-inch steel	48·0	1,152	11·0
Oleum (105 per cent. H_2SO_4) - -	2-inch steel	20·8	500	4·5
Gaillard 91 per cent. sulphuric acid.	2-inch steel	20·8	500	2·0
Strong nitric acid - - - -	3-inch lead	11·1	266	10·5
Weak nitric acid - - - -	2½-inch earthenware.	5·3	127	10·0

The figures in the last column are based on the amounts of acid required for 100 tons of TNT per day. No pipe-line should ever be in use more than 10 or 12 hours per day, otherwise serious delays occur in the event of a repair being needed.

As Grillo 98·6 per cent. sulphuric acid constitutes the sulphuric charge for both TNT and MNT mixes, it is consequently of paramount importance, as far as rate of production is concerned, that this acid should be run into the mixer as quickly as possible.

It should also be noted in connection with the lines which deliver the acids to be added to the sulphuric charge that a limit exists to the

rate at which they may be permitted to discharge acid into a mixer. This limit is set by :—

(a) *The rate at which the acid can be mixed with the acid already in the mixer.*—This case will be treated later (*see* page 66).

(b) *The rate of development of heat in the mix and also the rate of cooling effected.*—If it is desired to control the temperature of the mixing acids, it is advisable to restrict the flow of acids to the mixer in order to render impossible the undue development of heat. A 2 inch weak nitric acid line is ample in size, for example. Even with a line of this size it is not possible to run in the acid continuously, and a larger line might be even dangerous in the hands of a careless operative. This being so, if a single 2 inch line could not cope with the acid to be mixed, it would be better to instal an extra 2-inch line than to replace the 2-inch line with one of larger size. Speeding up is sometimes possible, however, even with nitric acid lines. The oleum line is on the same footing as the lines for nitric acids. Oleum is added to the mixes last of all, and the aim is to add it as slowly as possible; under these circumstances a slow delivery is an advantage.

Preliminary Mixing.

General Arrangement of preliminary Mixing Plant.—The accompanying illustration, Fig. 16, shows the arrangement of the acid-mixing plant on the TNT Acids Section at Queen's Ferry. The plant consists of 5 mild steel acid-mixing tanks,* each 10 feet diameter 5 feet mean depth, as detailed in Fig. 17. Each mixer is fitted with a stirring gear of the propeller type, and 4 mild steel cooling coils, the function of the latter being to take up the heat generated in mixing the acids. The vertical propeller shafts are driven by quarter twist belts from clutch pulleys on a line shaft driven by a belt from a motor; the line shaft runs practically the full length of the building. Cooling water is supplied from a 4-inch steel main clipped to the main stanchions of the building, and from which 2 inch branches are taken to a ring main encircling the top of each tank, connections from the ring main being made to each coil with a valve controlling the quantity of water through each coil. After passing through the coil the water is discharged into open funnel pipes and thence into ring mains encircling the tank foundations, these mains discharging into gutters in the floor. From each tank a 4-inch stoneware fume pipe is taken off to an 8 inch diameter fume main running the full length of the building, and supported on steel runners about 3 feet 9 inches high and spaced about 7 feet 6 inches centre to centre. This pipe is laid with a slight fall towards one end for drainage, and is connected to the fume system of the nitric-acid plant.

It should be noted that the strengths of acids and sizes of pipe lines indicated in Fig. 16 have in some cases been changed; these alterations are set out in the table on page 62. The main for 91 per cent. acid is clipped to the stanchions of the building as indicated in

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* This number was increased later to 7.

Fig. 16, whilst the other mains are carried on wooden trestles spaced 12 feet centre to centre. Two-inch branches are taken to each mixing tank from each of the five acid mains referred to above, the connections at the tanks being made with stoneware sockets. In all cases the inlet pipes must be taken well down into the tanks and allowed to discharge on to a stoneware tile supported from the bottom of the tank on a few bricks.

The outlets of the five mixing tanks are each controlled by a 3-inch cast steel valve, and are coupled together into 4-inch mains, one for MNT mixed acid and the other for TNT mixed acid. To the former are connected two 3-inch motor-driven Douglas pumps, one for operation and one for spare, and to the latter are connected three similar pumps, two for operation and one for spare. Cast iron cocks are connected to the suction and delivery end of each, in order that any pump may be cut out for repairs. These pumps discharge into 4-inch steel mains leading to the 20 feet × 12 feet final mixing or blending tanks (blenders).

The floors of the mixing and pump houses are of acid-proof brick laid in tar and fireclay, the mixing-house floor having a slight fall away from the pump house, and the floor of the latter having a slight fall away from the mixing tanks. The foundations of the latter are circular in form and consist of an outer wall of acid-proof brick filled in with brick rubble or concrete, a pocket being left in each foundation for the discharge pipe from the tank. Pump foundations are made to stand at least 6 inches above the floor line to protect the base of the pump from acid. In the case of the mixer, however, the solid base has the disadvantage of hiding any leakage of acid which may take place through the bottom of the mixer. Such leakage is most likely to take place through the bolt holes through which the mixing cylinder is bolted to the mixer base. This has actually happened in one or two cases, and necessitates cutting the concrete foundation away in order to replace the defective bolt. The foundation of one mixer was ultimately removed entirely and the mixer placed on steel girders resting on brick pillars, a practice which has since been followed in the erection of new plant.

The question naturally arises whether there is any other gain in the new arrangement other than that of rendering the base of the mixer easily accessible for observation and repair. The heat radiation losses have therefore been determined for a TNT mix made in a mixer resting (*a*) on steel girders and (*b*) on a concrete base. The mixer in each case was allowed to cool with the water shut off from the cooling coils.

(*a*) Fall in temperature in one hour was from 42·4° C. to 40·9° C. ∴ 1·5° C.

Temperature of outside air - = 6° C.
Weight of acid in mixer - = 18 tons.
∴ Heat radiated in one hour - = $18 \times 2{,}240 \times 1{\cdot}5 \times 0{\cdot}36$ C.H.U.
= 21,773 C.H.U.
Surface of mixer - - - = 316 square feet.
∴ Loss of heat per square foot per hour - - - - = 68·9 C.H.U.

(b) Fall in temperature in one hour was from 41·8° C. to 40·4° C. = 1·4° C.

Temperature of outside air - = 6° C.
Heat radiated in one hour - = 18 × 2,240 × 1·4 × 0·36 C.H.U.
= 20,321 C.H.U.
Loss of heat per square foot per hour - = 64·3 C.H.U.

It thus appears that the gain in cooling effect is almost negligible, since the 0·1° C. difference in fall of temperature is within the limits of experimental error.

Details of preliminary Mixers.—Fig. 17 shows some of the details of the acid mixing tanks. These are 10 feet diameter with a mean depth of 5 feet, and are provided with an internal stirring gear, consisting of a steel propeller working within a chamber. Above the chamber a disrupter is fitted to the vertical propeller shaft in order to break the core of all liquid emerging from the propeller chamber, a better mixing effect being thus obtained. The acid is discharged from the bottom of the tank through a 3-inch diameter elbow, to which is fitted a regulus metal plug-valve operated by a lever attached to the top of the tank. The top of the tank is completely covered by a steel cover, the latter being provided with a 15-inch diameter manhole and cover and the necessary inlets for the admission of sulphuric acid and weak and strong nitric acids. In addition to these openings a 4-inch diameter opening is made for the eduction of fumes from the acid, and also two glands are arranged for the passage of the plug-valve rods; these glands are packed loosely with asbestos fibre. Each tank is fitted with a gauge glass and cock, the connection between the gauge glass and the tank being controlled inside the latter by means of a small regulus metal plug-valve operated by means of a lever gear. The vertical stirrer shaft passes through the top cover of the tank, the aperture being closed by an acid seal. This seal is partially filled with sulphuric acid to prevent the admission of moist air to the contents of the tank.

The life of the wrought iron propeller is about 5 months. Observation of the propeller has shown that the blades become dangerously thin towards the end of this period, and cases are known where the premature destruction of the blades has been directly responsible for short life of the cooling coils. The state of the propeller is most important, therefore, from the point of view of rapidity and completeness in mixing, and also of wear and tear of plant, and its periodical inspection is most essential.

Considerations involved in preliminary mixing.—The aspects requiring consideration as regards the preliminary mixes are as follows:—

(1) The actual mixing together of the separate acids to produce a homogeneous mixed acid.
(2) The development of heat during the mixing of the separate acids.
(3) The removal of this heat.

Process of mixing the separate Acids.—There are two tests of the effectiveness of any method of mixing, viz.:—

(a) The nitric acid (particularly if it is weak) must be mixed into the sulphuric or partially mixed acid sufficiently quickly to prevent the serious corrosion of any part of the mixer, which might otherwise result from its contact with unmixed nitric acid.

(b) The mix must become uniform in composition as rapidly as possible.

The first point is quite as important as the second. For example, it is quite possible in practice to add the nitric acid at a faster rate than the mixing can cope with. Attempts to speed up the mixing by running nitric acid simultaneously from the strong and weak nitric acid mains have proved quite unsatisfactory, as the mixing arrangement is not efficient enough to mix the double bulk of nitric acid at once. Nitrous fumes from the fume-stack bore witness to the corrosion that was taking place, but the fuming ceased immediately when the supply of either strong or weak nitric acid was shut off.

The mixing gear.—Rapidity in producing uniformity of composition is brought about almost entirely by the propeller, the dimensions of which are given below. The mixing cylinder, the top of which is 34 inches from the mixer bottom, serves to direct the rising stream of acid, and an impeller (disrupter) on the same vertical shafting as the propeller, 16 inches from the top of the mixer, is set very roughly so as to beat the acid down, and serves mainly to break up the acid currents due to the propeller, which might otherwise prove too symmetrical. This would certainly prevent anything in the nature of a thorough mixing.

It is the impeller which is mainly responsible for the first stage in mixing; the propeller would give by itself stream-lines of unmixed nitric acid. The impeller renders the mixing far more turbulent, and thoroughly beats the surface acids together. The fact that streams of unmixed nitric acid are actually carried up through the mixing cylinder, especially when the upper level of the acid in the mixer is between 34 and 44 inches, *i.e.*, below the impeller, is shown by the fact that several lead coils have been "holed" about the level of the top edge of the mixing cylinder on the sides facing the latter.

Rate of mixing.—A very useful figure is obtained by determining the time taken for the total contents of the mixer to pass through the mixing cylinder. This is arrived at as follows:—

Radius of propeller - - = $7\frac{1}{4}$ inches.
Pitch of propeller - - - = $18\frac{1}{2}$ inches.
Volume of acid raised during one revolution - - - = $\frac{22}{7} \times (7\frac{1}{4})^2 \times 18\frac{1}{2} = 3{,}056$ cubic inches.
Allowing 10 per cent for slipping[1] - - - = 306 cubic inches.

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[1] Using this type of stirrer, the actual figure is probably nearer 30 per cent.

Volume of acid actually mixed per revolution - - = 2,750 cubic inches.
Speed of stirrer - - - = 200 r.p.m.
Volume of acid raised per minute - - - - = 550,000 cubic inches
Dimensions of mixer - - = 10 feet diameter × 5 feet deep.
Volume of acid in a full mix (say, of 4 feet 6 inches dip) $= \frac{22}{7} \times (5)^2 \times 4\frac{1}{2}$ cubic feet = 354 cubic feet.

Time required for a complete circulation $= \frac{354 \times 1728 \times 60}{550,000}$ = 67 secs.

Practice shows that nine circulations, with the help of the impeller motion, give a uniform mix, the required time being 10 minutes. Under no circumstances is a mix allowed to be pumped away until at least 10 minutes after the last of the nitric acid has been added.

The velocity, ignoring slip, of the acid through the propeller chamber is:—

Pitch of propeller - - - - $18\frac{1}{2}$ inches.
Speed of stirrer - - - - 200 r.p.m.
Velocity of acid through propeller chamber - - - - - $\frac{18\frac{1}{2} \times 200}{60 \times 12}$ = approximately 5 feet per second.

This rate is sufficiently rapid to be seriously interfered with if there is not enough free space between successive turns in the cooling coils of the mixer. It is quite clear that the coils present a certain resistance to the flow, and in the case of one consignment of coils received the space between successive coils and the free space between the lowest coil and the bottom of the mixer were too small. As a result, the coils showed distinct signs of being scoured by the stream of circulating acid. The free space from the lowest coil to the bottom of the mixer was in this case only $2\frac{1}{2}$ to 3 inches, and the lowest four or five coils were eventually worn away beyond hope of repair. It is found advisable to allow at least 6 inches of free space below the lowest coil, and the distance between successive turns should be, as a minimum, $1\frac{3}{8}$ inches.

Development of heat during mixing.—The control of the temperature of the mixing acids forms a problem of great importance. In practice this resolves itself into balancing the safety of the plant against the speed in mixing. From the latter point of view it would seem advisable to permit the heat to develop as rapidly as possible, since the rate of cooling is approximately in inverse ratio to the difference between the temperatures of the mixing acids and the cooling water. From the point of view of plant safety, however, a limit must be set upon the maximum temperature which the mixing acids may be permitted to reach. This follows for two reasons, viz., to decrease corrosion of the mixers and coils, and to avoid loss of nitric acid through overheating of the mixed acid. In practice, the upper limit of the temperature which mixing acids are allowed to attain is taken as approximately 40° C.

The heat developed during the mixing of acids may be said to be due to the levelling up of the dilutions of the acids mixed. If two sulphuric acids are mixed, their dilutions are equalised; but when nitric acid is mixed with sulphuric acid, the mixture can hardly be regarded as one of nitric acid and sulphuric acid of equal dilutions. The dilution of the latter must certainly be regarded as the greater of the two. The heat developed, as found by experiment, occupies an intermediate position between that which would be developed by an actual equalising of the two dilutions, and that which would be developed if all the water were combined with the H_2SO_4, leaving the nitric acid as HNO_3 of 100 per cent. strength.

The manner in which the heat develops is most readily grasped by considering what would happen if the mixes were made in the absence of cooling of any kind.

"*Characteristic*" *temperature of a mix.*—A distinguishing feature of all mixes made without cooling of a sulphuric acid with another sulphuric acid or with a nitric acid of higher dilution is the fairly rapid attainment during the addition of the first few tons of the weaker acid of a more or less *high temperature*. This temperature remains practically constant during the addition of the remaining acid.

The following examples of miniature mixes made in a beaker illustrate this point quite clearly.

Example I.—Mixture of 98·5 per cent. sulphuric with nitric acid of approximately 50 per cent. strength.

Temperature of nitric acid 21·7° C.

Acid.			Temperature attained.	Temperature after correction for radiation loss.
98·5 per cent. sulphuric acid.		50 per cent. nitric acid.		
c.c.		c.c.	° C.	° C.
400		—	22·2	22·2
400	+	50	62·5	62·5
400	+	100	74·5	78·0
400	+	150	82·0	87·7
400	+	200	87·5	94·0
400	+	250	90·0	98·0
400	+	300	90·2	99·7
400	+	350	89·2	101·7
400	+	400	88·0	102·0

It is quite obvious, therefore, that it would not be practicable to permit the attainment of the temperature indicated. But, as will be seen later, the figure is extremely useful to the acids mixer in indicating to him the essential difficulties to be overcome.

Example II.—Mixture of 98·5 per cent. sulphuric acid with 89·0 per cent. nitric acid.

Temperature of nitric acid 21·8° C.

Acid.			Temperature attained.	Temperature after correction for radiation loss.
98·5 per cent. sulphuric acid.		89 per cent. nitric acid.		
c.c.		c.c.	° C.	° C.
400		—	22·2	22·2
400	+	50	50·0	50·3
400	+	100	54·4	55·1
400	+	150	55·3	56·3
400	+	200	56·9	57·4
400	+	250	55·8	57·6
400	+	300	55·6	57·7
400	+	350	55·0	57·5
400	+	400	54·7	57·5

The figures given above, which were obtained by mixing the volumes of acids mentioned in a 1,000 c.c. beaker and making a simple radiation correction, may be regarded as correct to within 2°–3° C.

It is obvious from the two examples given, and it follows directly from a theoretical consideration of the heats of dilution of sulphuric and nitric acids, that the temperature attained is higher the greater the difference between the dilutions of the sulphuric and nitric acids.

The comparative steadiness of the maximum temperature attained is due to the fact that when that point has been reached, the heat evolved by the addition of further nitric acid is just sufficient to raise its temperature to that of the rest of the mix.

This temperature may reasonably be called the *characteristic* temperature of the mixture concerned. It can be found very easily, as has been described, and when obtained it is an indication of—

(1) The amount of cooling surface desirable to cope with the heat evolved by the mix.

(2) The time required to complete the mix and reduce the temperature to one suitable for pumping.

(3) The difficulty of maintaining at a low figure, by cooling and other means, the maximum temperature attained during mixing.

It is necessary, however, to distinguish plainly between—

(*a*) The characteristic temperature of a mix, which is the temperature which would be attained if the second acid were added in the absence of any cooling whatsoever; and

(*b*) The actual temperature attained during practical mixing, which depends upon the efficiency of cooling and the rate at which the second acid is added.

The characteristic temperature of any mix is not absolutely constant, but varies with the initial temperatures of the unmixed acids. The *heat-rise* is the constant factor, and some might prefer to call this the characteristic feature of the process. It is, however, more convenient for the acids mixer to think of the upper limit of temperature which can be reached; this can be made a constant by expressing it in terms of acids, the initial temperature of which is an average, say, 20° C.

Effect of the characteristic temperature upon mixing.—The higher the characteristic temperature the greater the difficulty in keeping at a low figure the maximum temperature attained during mixing. The difficulties due to high temperatures greatly increased after the reduction in water content of TNT mixed acid from 4·6 per cent. to 2·7 per cent. In the former case the acid was mixed almost entirely from Grillo 98·6 per cent. sulphuric acid and retort strong nitric acid of about 90 per cent. strength. Under these circumstances the characteristic temperature did not exceed 50° C., and consequently the difficulty of overheated mixes did not arise. The revised specification for TNT mixed acid means, in effect, the replacement by oleum of 25 per cent. of the 98·6 per cent. acid formerly used. The characteristic temperature of a mix consisting of oleum and strong nitric acid considerably exceeds 100° C., and in order to keep down the temperature of these mixes the oleum is added last of all and in small quantities at a time to the otherwise completed mix.

Another factor which increased these difficulties was the higher working efficiency at the denitration plant. This resulted in the production of greater quantities of weak nitric acid, which it was necessary to reintroduce into the acids cycle in the form of MNT mixed acid. For, whereas the latter was formerly composed of Gaillard 90 per cent. sulphuric acid and retort weak nitric acid of 70 per cent. strength, it afterwards became necessary to mix Grillo 98·6 per cent. sulphuric acid with 50 per cent. nitric acid recovered at the denitrators. The effect of this was to raise the characteristic temperature of MNT mixes from 35° C. to a temperature approaching 100° C. The former mixes needed little, if any, cooling; the latter need prolonged cooling, and cautious addition of nitric acid.

Thus, both changes have operated in the same direction, viz., to throw an increased burden upon the cooling capacity of the mixing plant.

Cooling of mixes.—This involves the consideration of—

(1) The total amount of heat to be removed from the mixed acids.

(2) Sources of cooling, including a consideration of the relative merits of steel and lead coils

(3) Factors determining the rate of cooling.

It is convenient to deal first with the factors determining the rate of cooling. These are, apart from the cooling capacity of the coils used, briefly as follows :—

(1) The maximum temperature permitted during the progress of a mix.

(2) The temperature at which a mix is considered to be cool enough for pumping to the blenders.

Maximum temperature attained during mixing.—Supplementing what has already been said on this subject, it is clear that, with a plant working at its full capacity, mixes must of necessity attain a higher temperature in summer than in winter, since this temperature depends upon—

initial temperature of the acids mixed, which may vary as much as 20° C.

(*b*) The temperature of the cooling water, which may vary 8° or 9° C.

(*c*) The heat liberated in the course of mixing, which is the only constant factor.

If it is insisted that the same maximum temperature shall obtain winter and summer alike, then the time taken to cool will be as much as 25 per cent. greater in summer than in winter.

The really important point is to standardise the maximum temperature and keep all mixes as close as possible to this maximum temperature from beginning to end of the mixing process. The temperature should be fixed as low as is compatible with mixing off the requisite quantities of acids. Uniformity of temperature in mixing is the ideal.

Temperatures at which Acid may be pumped.—This depends upon two factors :—

(a) *The maximum temperature* at which mixed acid may be received at the nitration houses; this is about 25° C. At one time 35°–40° C. was regarded as a suitable pumping temperature, and experience showed that acid pumped into the blenders at 35°–40° C. reached the nitration houses at a satisfactory temperature, radiation losses in the blenders, pipe-lines, and storage tanks being responsible for the drop in temperature. This was not the case later however, as the speeding up of the process reduced the time which elapsed during the progress of the mixed acid from the mixer to the nitrating vessels.

(b) *Variation of corrosion with temperature.*—This point is important and has made itself felt mainly in connection with the pumping of acid. Until the pumping temperature was reduced, constant trouble was experienced through the seizing of the pumps. It is now taken as about 25° C. No acid is ever pumped from a mixer at a temperature exceeding this, and very little pump trouble has been experienced since the introduction of this rule.

Total amount of heat to be dissipated.—This can now be found. The calculation will be made in terms of the amount of heat to be removed per week, on the basis of an output of 700 tons of TNT per week.

TNT mixed Acid.

Tonnage of acids mixed = 700 × 4·8 = 3,360 tons.

The heat-rise was determined experimentally by mixing together in a beaker relative quantities of the acids required.

Heat-rise = 20° C. to 77° C.

The acid is cooled to 25° C. before pumping it away to the blenders. Hence, the heat to be removed is equivalent to the heat which the mixed acid would give out in cooling from 77° C. to 25° C., *i.e.*, 52° C.

Specific heat of TNT mixed acid = 0·36.

∴ Heat to be dissipated - - = 3,360 × 2,240 × 52 × 0·36 C.H.U.
= 140,900,000 C.H.U.

MNT mixed Acid.

Tonnage of acid mixed = 700 × 1·62 - - = 1,134 tons.

Heat-rise (determined experimentally as before) = 20° C. to 99° C.

Heat to be removed is equivalent to the heat which the mixed acid would give out in cooling from 99° C. to 25° C. = 74° C.

Specific heat of MNT mixed acid = 0·46.

∴ Heat to be dissipated - - = 1,134 × 2,240 × 74 × 0·46 C.H.U.
= 86,470,000 C.H.U.

The number of mixers allotted for the mixing of each mixed acid should naturally be proportional to the relative amount of heat to be dissipated in the case of each acid. Thus, with seven mixers available, the best arrangement is to use three for MNT mixed acid and the remaining four for TNT mixed acid.

Total heat to be dissipated.

Total heat to be dissipated per week = (140,900,000 + 86,470,000) C.H.U.
= 227,370,000 C.H.U.

∴ Heat to be dissipated per day (for a 6-day week) - - - - = approximately 38,000,000 C.H.U.

Sources of cooling.—These are two in number :—

(1) The loss of heat through radiation and conduction from the mixer itself.

(2) The heat removed by the water passing through the cooling coils.

Heat lost by radiation from the Mixer.

This quantity has been determined by allowing a mix to cool down with the water shut off from the cooling coils.

∴ Fall in temperature in one hour was from 42·40 to 40·90° C. = 50° C.

Temperature of outside air - = 6° C.
Weight of acid in mixer = 18 tons of TNT mixed acid.
∴ Heat radiated in one hour - = 18 × 2240 × 1·5 × 0·36 C.H.U.
= 21,773 C.H.U., say 22,000 C.H.U.
Surface of mixer - - - = 316 square feet.

∴ Loss of heat per square foot of surface per hour $= \frac{21773}{316} = 68 \cdot 9$ C.H.U.

The heat lost in this way is approximately 6½ per cent. of the total heat removed during mixing.

Heat removed by the Water of the Cooling Coils.

At the time of the closing down of the Queen's Ferry mixing plant, five of the seven mixers were fitted with lead coils and two with steel coils. It is therefore necessary to ascertain the cooling efficiency of each type of coil.

(a) *Lead coils.*—In order to determine the cooling efficiency of the lead coils in use, the rate of cooling was determined for two standard mixes, viz., for—

(i) 18 tons of TNT mixed acid, and for
(ii) 16·5 tons of MNT mixed acid.

The first of these determinations was made in a mixer provided with four lead coils, and the latter in a mixer with three lead coils, the fourth coil having been disconnected on account of leakage.

(a) The results of the TNT mixed acid have been tabulated as follows:—

Time.	Temperature of mixed acid.	Final temperature of cooling water.	Time.	Temperature of mixed acid.	Final temperature of cooling water.
Min.	°C.	°C.	Min.	°C.	°C.
0	42·2	20·0	18	34·8	—
2	41·1	—	20	34·1	15·0
4	40·5	19·0	22	33·0	—
6	39·7	—	24	32·8	14·8
8	38·7	18·0	26	32·1	—
10	37·8	—	28	31·5	14·0
12	37·2	17·0	30	30·8	—
14	36·4	—	32	30·0	13·5
16	35·7	16·0	—	—	—

Temperature of cooling water on entering coils = 2° C. 18 tons of TNT mixed acid were cooled down from 42·2° C. to 30° C. in 32 minutes using four coils.

Heat given out by this quantity of acid - = 18 × 2,240 × 0·36 × 12·2.
= 177,085 C.H.U. in 32 minutes.
= 332,000 C.H.U. per hour (approximately).

Fall in temperature due to radiation - - - - = 22,000 C.H.U. per hour.
∴ Heat transferred to cooling water - - - - = (332,000–22,000) C.H.U.
= 310,000 C.H.U. per hour.
∴ Each coil accounts for $\frac{310,000}{4}$ - - - - = 77,500 C.H.U. per hour.

(*b*) Results for MNT mixed acid :—

Time.	Temperature of mixed acid.	Final temperature of cooling water.	Time.	Temperature of mixed acid.	Final temperature of cooling water.
Min.	°C.	°C.	Min.	°C.	°C.
0	41·7	16·5	24	35·0	13·5
2	41·5	—	26	34·5	—
4	40·9	16·0	28	34·0	13·4
6	40·3	—	30	33·5	—
8	39·8	15·5	32	32·7	13·0
10	39·0	—	34	32·5	
12	38·5	15·0	36	32·2	12·9
14	37·9	—	38	31·9	—
16	37·3	14·4	40	31·2	12·8
18	36·7	—	42	30·8	—
20	36·0	14·0	44	30·4	12·7
22	35·3	—	46	30·0	—

Temperature of cooling water entering coils - - - - - - = 2° C.

16·5 tons of MNT mixed acid were cooled down from 41·7° C. to 30° C. in 46 minutes with the use of the coils.

Heat given out by this quantity of acid - - - = 16·5 × 2,240 × 0·46 × 11·7 C.H.U.
= 198,918 C.H.U. in 46 minutes.
= approximately 259,500 C.H.U. per hour.

Fall in temperature due to radiation - - - - = 22,000 C.H.U. per hour.
∴ Heat transferred to cooling water - - - - = (259,500 — 22,000) C.H.U.
= 237,500 C.H.U. per hour.
∴ 1 coil accounts for $\frac{237,500}{3}$ - = 79,000 C.H.U. per hour.

This result agrees with the first to within the limits of experimental or.

The summarised data for lead coils may be taken as follows :—

Number of turns	14
Diameter (centre to centre)	36 inches.
Height of top turn from bottom of mixer (*i.e.*, depth of acid necessary to submerge coil completely)	46 inches.
Approximate surface of one lead coil	70 square feet.

From above, the average rate of dissipation of heat per lead coil is 78,250 C.H.U. per hour.

Cooling efficiency per square foot of surface is therefore approximately 1,120 C.H.U. per hour.

This result applies, however, only to one particular temperature gradient between hot mixed acid and cooling water (the average temperature of the mixed acid in the above cooling experiments was 36° C.; final temperature of cooling water was 20° C.).

Hence, it may be assumed with a fair amount of accuracy that if the temperature of the mixed acid be kept at 36° C. during the process of evolution of heat, then with cooling water at an initial temperature of 2° C. the loss of heat per coil per hour would be 78,250 C.H.U. as shown.

In summer, the average initial temperature of the cooling water is 12° C. To secure the same cooling effect from the coils it would be necessary to raise the permissible temperature of the mixing acids 10° C., *i.e.*, to 46° C. All the subsequent calculations are on the basis of a difference in temperature of 34° C. between the acid and the cooling water.

If 40° C. be taken as the permissible temperature, the rate of loss of heat per coil-hour would be roughly

$$\frac{78{,}250 \times (40 - 12)}{(46 - 12)} \text{ C.H.U.,}$$

assuming that the rate of loss of heat is proportional to the difference in temperature between the acid and the cooling water.

The rate of loss of heat then becomes 64,440 C.H.U. per coil-hour, a reduction of 17·6 per cent., which is substantial.

(*b*) *Steel coils.*—In order to arrive at the data required, a TNT mixed acid was cooled down in a mixer provided with steel coils. The results of the experiment are tabulated overleaf.

Time.	Temperature of mixed acid.	Final temperature of cooling water.	Time.	Temperature of mixed acid.	Final temperature of cooling water.
Min.	° C.	° C.	Min.	° C.	° C.
0	44·0	26	22	35·5	20
2	43·0	26	24	34·5	20
4	42·5	25	26	34·0	20
6	41·5	24	28	33·5	19
8	40·5	24	30	33·0	19
10	40·0	23	32	32·0	18
12	39·0	23	34	31·5	18
14	38·0	23	36	31·0	17·8
16	37·5	22	38	30·5	17·7
18	36·5	22	40	30·0	
20	36·0	21			

Temperature of the cooling water entering the coils = 2° C.

Heat given out by 18 tons of TNT mixed acid in cooling from 44° to 30° C.

= 18 × 2240 × 0·36 × 14 C.H.U. in 40 minutes.
= 304,819 C.H.U. per hour.

Heat lost by radiation from mixer = 22,000 C.H.U. per hour.

∴ Heat transferred to cooling water
= (304,819 − 22,000) C.H.U. per hour.
= 282,819 C.H.U. per hour.

Heat dissipated per coil-hour $= \frac{282,819}{4} =$ 70,700 C.H.U. per hour.

Four steel coils represent 320 square feet of cooling surface.

Hence, cooling power per square foot of surface
= 880 C.H.U. per hour.

Comparison of Steel and Lead Coils.—The results obtained for the two types of coil are compared in the following table :—

Temperature gradient approximately 36° − 2° C.

——	Steel coils.	Lead coils.
1. C.H.U. removed per coil-hour - - -	70,700	78,250
2. C.H.U. removed per square foot of surface per hour.	880	1,120
3. Rise of temperature of cooling water (mixed acid being at 36° C.)	19° C.	11° C.
4. Consumption of water per coil-hour - -	1·7 tons	3·2 tons

For the respective sizes of the coils used in the above experiments, therefore, the total cooling capacity of a lead coil is about 10 per cent. greater than that of a steel coil. The chief reason for this is the smaller internal diameter of the latter, which seriously restricts the rate of flow of water through the coil. In addition to this, in the experiments cited above, the flow was further reduced through water being supplied to the steel coils at a considerably reduced pressure. From the point of view of cooling efficiency, however, steel coils are preferable to lead coils. The other factor which determines the class of coil most suitable for use is that of wear and tear. It is certainly not worth while installing steel coils merely as regards cost, unless their life is at least three times that of lead coils. The average life of the lead coils is about 3½ months, and it is anticipated that by careful working this period may be prolonged to five months, although it is doubtful whether the latter figure can be exceeded. Three coils which were removed after five months' constant use had worn dangerously thin in places, and were quite beyond repair. It appears probable that steel coils will prove the most economical for TNT mixed acid, but there is very little data on this point at present. Lead coils are undoubtedly preferable for MNT mixed acid, and in fact for cooling any mix utilising weak nitric acid. In the event of any sudden stoppage of the stirrer whilst weak nitric acid is being run into the mixer, steel coils are seriously attacked at once, but lead coils resist attack much more satisfactorily. Again, if through any reason (*e.g.*, leakage of a cooling coil) the dilution of MNT mixed acid, which is already high, should exceed 20 per cent., corrosion of lead coils is comparatively slight, but steel coils may be destroyed by a single experience of this kind.

Steel cooling coils were successfully used at H.M. Factory, Gretna, in the nitroglycerine acid mixers. The coils are constructed of drawn mild steel, 1½ to 1¾ inches internal diameter and $\frac{3}{16}$ to ¼ inch in thickness, Each coil has 13 turns, and is supported at equal distances by four iron standards bolted together. The cooling surface of each coil is 9,750 square inches and the total length 1,620 inches. The coils stand 4 feet high and are 3 feet in diameter, with inlet and outlet protruding through the lid of the mixer leaving screen and socket for the connection to the water main. Experience has shown it to be necessary to jacket these coils where the inlet and outlet arms protrude through the lid. This prevents fumes, which give rise to weak acid, from corroding the coil. Coils which have "holed" at the welds are repaired by rewelding and jacketing in a similar manner, mild steel jackets being used in each case.

Causes and prevention of wear and tear of coils.—When the plant was first operated, in addition to wear and tear from legitimate causes, a certain amount of destruction of coils was directly attributable to one or more of the following causes:—

(1) Faulty arrangement of the inlets of acid pipe-lines to mixers.—In many cases the incoming stream of acid impinged directly on to a coil, resulting in a rapid holing of the coil at that point. Distribution of the acid inlets between the four coils is preferable to centralising them in one or two coils.

(2) Leakage of nitric acid into a mixer below the mixing level, or when the mixing gear was not operating; failure to start

the stirrer before commencing to add nitric acid; failure of the stirring gear through any cause. These difficulties have been largely overcome by dispensing with the friction clutches originally installed, and allowing the stirring gear to operate continuously. As previously mentioned, no mixer is now allowed to remain empty, and a charge of 24½ inches of sulphuric acid is run in immediately the contents of the mixer have been pumped to the blending tank.

(3) Bringing hot oleum into contact with the lead cooling coils.—This is now avoided by adding the oleum last of all the acids required for the mix.

Mention has also been made of another feature of coil wear and tear, viz., the holing of coils on a level with the top of the mixing cylinder on the side of the coils nearest the cylinder. An attempt has been made to prevent this by protecting coils at this level with narrow strips of lead on the sides of the coils facing the cylinder.

Cooling capacity of mixing plant.—The total amount of heat to be dissipated per day was shown on page 72 to be 38,000,000 C.H.U.

To remove this heat there are seven preliminary mixers, five of which are provided with lead coils and two with steel coils.

Heat removed per hour by five mixers each with four lead coils = 20 × 83,750 = 1,675,000 C.H.U.

Heat removed per hour by two mixers each with four steel coils = 8 × 76,500* = 609,600 C.H.U.

Total heat removed per hour by seven mixers = 2,284,600 C.H.U.

In order to cool the mixed acid required for 700 tons of TNT per week, therefore, the coils will be required to work effectively for 16½ hours per day. This leaves 7½ hours to cover the "dead" time of mixing, and it will allow one mixer at a time to be out of action for repair. Incidentally, this margin will just permit the maximum permissible temperature in summer to be kept as low as 40° C.

Water required for cooling purposes.

5 mixers each with 4 lead coils require 3·2 × 5 × 4 - - =	64·0 tons of water per hour.
2 mixers each with 4 steel coils require 1·7 × 2 × 4 - - =	13·6 ,, ,, ,,
Total requirements per hour for 7 mixers - - - =	77·6 tons.
Amount of water required per day 77·6 × 16½ - - - =	1,280 ,,
Assuming summer requirements to be 20 per cent. above this tonnage of water required per day - - =	1,536 ,,

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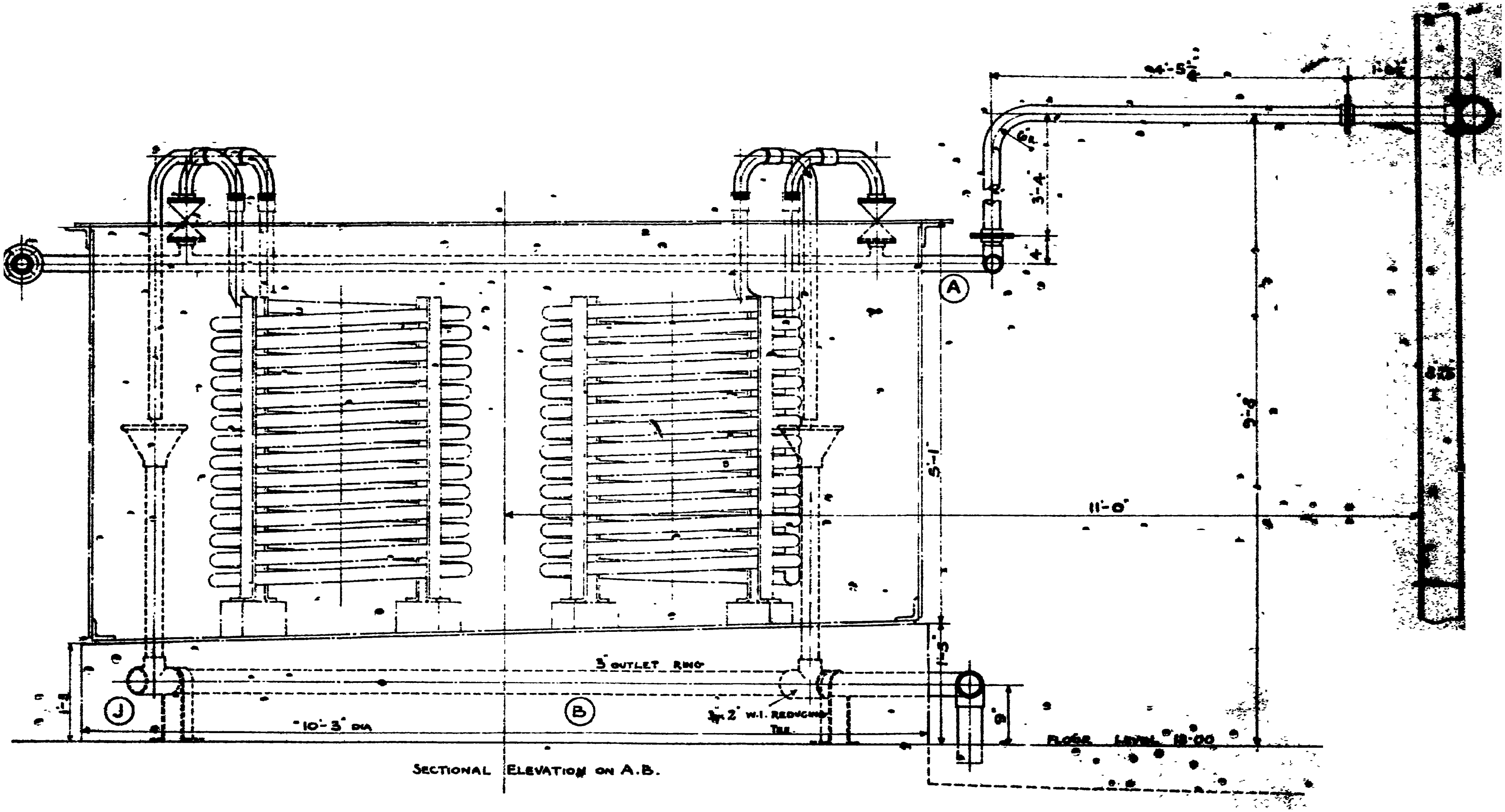
* The figures taken above for heat removed by each coil include 5,500 C.H.U., which is one quarter of the total radiation loss from the surface of the mixer.



SECTIONAL ELEVATION ON A.B.

FIG.18

15327/944/79.500.721.

The 4-inch main installed can deliver up to 1,750 tons per day, which thus gives a margin of about 200 tons per day.

Water supply to preliminary mixers.—Fig. 18 gives a general idea of the arrangement of the water supply pipes at the preliminary mixing plant. A 4-inch main is run the full length of the mixing house, and is clamped to the main stanchion at a height of 9 feet 8 inches above the floor level. From this main a 2-inch branch is taken off at each mixer, and is connected to a 2-inch ring main encircling the top of each tank. From this ring main 1½-inch connections, each controlled by a gate valve, are made to each coil, the water entering at the bottom of the coil and leaving at the top, whence it is discharged into a cast iron funnel at the top of a 2-inch stand pipe. The discharge being open, it is thus possible readily to adjust the flow of water to each coil to obtain the requisite cooling effect. The four 2-inch stand pipes at each mixer connect to a 3-inch discharge ring main round the tank, and this in turn discharges into a gutter in the floor of the mixing house and thence away to the nearest drain. The stand pipes are cleated to the side of the tank, and the discharge ring mains are supported off the floor on wooden chocks with straps over the pipes.

BLENDING.

General Arrangement of Blending Tanks.—The blending plant consists of four steel tanks, 20 feet diameter by 12 feet deep, supported on foundations of brick and steel. The acids from the preliminary mixers are brought to the top of the mixing tanks by means of 4-inch mild steel pipes with 4-inch cast iron plug-cocks inserted to control the feed of acid into the tanks, the main feeding the TNT tanks being connected to that serving the MNT tanks, so that if necessary MNT acid may be blended in one of the TNT tanks. The discharge from each tank is 3 inches in diameter, and is controlled by a 3-inch cast steel Quinan valve. Immediately after passing the valve the discharge pipe is increased to 4 inches in diameter, and the TNT acid discharges are led into one 4-inch main and the MNT acid into another 4-inch main. From these mains the acid is pumped to storage by means of 3-inch motor-driven Douglas pumps. In the event of a breakdown of the pumps the acid can be gravitated into either of two blow-casks (Fig. 21) set in a pit outside the blending house, and by means of which the acid can be blown up into the storage tanks. The walls of the pit are of brick, and are extended 1 foot above ground level at the top to prevent surface drainage from gaining access thereto. The pit is covered with loose wood boarding as shown.

The building housing the plant consists of a main span, 26 feet wide by 73 feet long, which houses the mixing tanks, with a lean-to span 10 feet wide by 54 feet 9 inches to house the pumps. The building is of timber throughout and is provided with wooden gangways over the tanks for giving access to inlet valves, &c., and with motor platforms. In the roof of the lean-to over the pumps a 7-inch by

4-inch rolled steel joist is installed to serve as a track for lifting tackle for removing pumps when necessary, the track girder being carried by bent angles bolted to the rafters of the lean-to roof. The pump-house floor is of acid-proof brick laid in tar and fireclay, and the floor level of the blending house is 6 inches above the surrounding ground level and is paved in a similar manner to the pump house.

The general arrangement of one blending tank is shown in Fig. 19.

Details of Blending Tank.—The blender is 20 feet diameter by 12 feet deep inside, and is built up entirely of $\frac{5}{8}$-inch steel plates with double riveted lap joints, the side plates being connected to the bottom plates by means of a 5-inch by 5-inch by $\frac{5}{8}$-inch steel angle (Fig. 20). The top is encircled by a $3\frac{1}{2}$-inch by $3\frac{1}{2}$-inch by $\frac{1}{2}$-inch angle ring, and is provided with a cover of $\frac{5}{8}$-inch steel plates which are attached to the angle ring by means of $\frac{3}{4}$-inch bolts. The cover is built up of 12 radial plates with single-riveted lap joints, and a central plate, 7 feet in diameter, in the centre of which is a hole 3 feet $7\frac{1}{2}$ inches in diameter. The cover is provided with an internal drip ring formed by a $2\frac{1}{2}$-inch by $2\frac{1}{2}$-inch by $\frac{5}{16}$-inch angle riveted on, and with a 15-inch diameter manhole frame and cover. The manhole frame, which is of cast iron, is made with a recess about $2\frac{1}{2}$ inches deep in which rests a cover of $\frac{1}{8}$-inch steel plate. The recess is filled with sulphuric acid which forms a seal, so that moisture shall not obtain access to the tank. In addition to the above, each cover is provided with two $5\frac{1}{2}$-inch openings for admitting the pipes supplying 98·6 per cent. sulphuric acid and 20 per cent. oleum, and one $6\frac{1}{2}$-inch opening for the admission of the mixed acid pipe. One mild steel patch for the connection of an air vent pipe is also provided The tank is fitted with a 3-inch bottom discharge closed by a regulus metal plug-valve.

Agitation of the contents of the blender is effected by means of a propeller working within a cast iron chamber, as in the preliminary mixer. The propeller is attached to a vertical shaft $2\frac{1}{2}$ inches in diameter, the lower end of which works in a footstep bearing, whilst the upper end passes through the tank cover and revolves in a cast iron bearing attached to the cast iron plate closing the central aperture of the tank cover. The weight of the shaft, &c., is carried by a ball thrust washer placed immediately above the top bearing, a split grip collar being placed on the shaft immediately above this washer. In setting the shaft in position, care must be taken that the shaft is supported on the thrust washer and not on the footstep bearing. The shaft is rotated by means of a keyed-on pulley, 27 inch diameter by [illegible] inch face, this giving a speed of 150 r.p.m. to the shaft. An oil drip tray is clamped to the shaft immediately below the top bearing, and in this tray is caught any oil which leaks from the bearing. In order to prevent moist air from entering the tank the opening through which the shaft passes through the tank cover is provided with an acid seal consisting of a cast iron bell attached to the shaft, which rotates in sulphuric acid contained in a receptacle formed in the cover. The mixing propeller is 24 inches diameter by 30 inches pitch, and the chamber in which it works is 2 feet 2 inches inside diameter by 5 feet

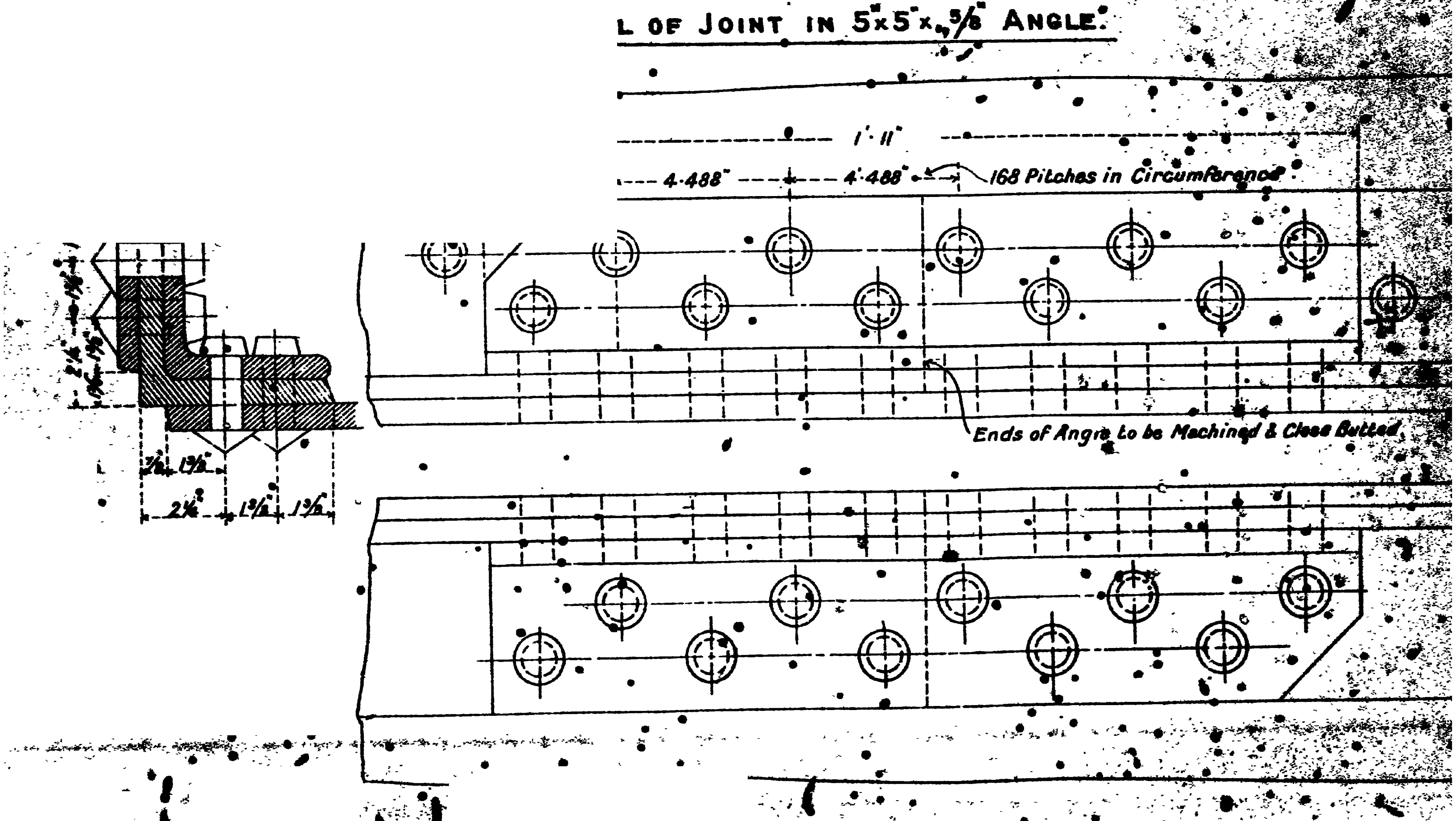

L OF JOINT IN 5"×5"×5/8" ANGLE.
1'·11"
4·488"
4·488"
168 Pitches in Circumference.
Ends of Angle to be Machined & Close Butted.
7/8"
1 3/8"
2 1/4"
1 3/8"
1 3/8"

FIG. 20.

long, being supported from the tank bottom by means of three angle steel legs so that the lower edge of the chamber is 12 inches above the tank bottom. Just above the top of the chamber is fitted a disrupter consisting of twisted 3-inch by ⅜-inch flat bars nipped to the shaft. This disrupter serves to break up the core of liquid lifted by the propeller, thus causing a better mixing effect.

Details of blow-cask for mixed acid.—Each blow-cask (Fig. 21) is 4 feet 6 inches diameter by 19 feet long, and is built up of ⅝-inch mild steel plates as to the shell, and $\frac{11}{16}$-inch plates as to the ends, the latter being pressed out spherical to a radius of 4 feet 6 inches. Circumferential joints are single-riveted, and longitudinal joints are double-riveted, all rivets being ¾ inch diameter and 2⅝ inches pitch. Each blow-cask is fitted with a cast steel manhole frame and cover, two 4-inch diameter inlet stools, two 4¾-inch diameter outlet stools, and one 1-inch diameter air inlet stool, all stools being of cast steel with machined faces.

Processes occurring in the Blending Tanks.—These are four in number:—

(1) Mixing a bulk of from 120 to 150 tons of acid, most of which has previously passed through the preliminary mixers, in order to obtain a mixed acid of uniform composition.
(2) Doping this mixture to secure a blend the analysis of which falls within the given specification.
(3) Development of a certain and sometimes considerable amount of heat.
(4) Loss of heat by radiation, supplementary to that lost in the preliminary mixers.

Mixing.—Two methods of mixing are available:—

(*a*) By means of a larger propeller and impeller of the same type as those employed in the preliminary mixers. The top of the mixing cylinder is 6 feet from the bottom of the blender, so that it is not possible to mix, by this method, a blend of less than 6 feet in depth.
(*b*) By means of compressed air issuing from a series of holes in a circular coil resting on the bottom of the blender.

Experience has shown that the former method is quite adequate in itself; supplementary mixing by means of compressed air, although resorted to regularly at one time, has proved to be wholly unnecessary. This does not mean, however, that the compressed-air installation is altogether superfluous, for upon occasion, although rarely, the ordinary mixing gear has been out of action, and compressed air alone has then been employed as a means of mixing, proving quite satisfactory. Compressed air is also useful in mixing when the depth of the acid in a blender is below 6 feet.

The time needed to mix satisfactorily a blend of 140 to 150 tons using air agitation is about 40 minutes.

Time required for thorough mixing.

Experiment and repeated trial have shown half-an-hour to be the minimum safe time for the attainment of uniformity of composition by means of mechanical agitation, as indicated by repeated analyses after continuous mixing and periodical sampling. As former practice prescribed mixing for at least two hours and even longer if time permitted, the reduction of this period to half an hour has saved 1½ hours in the time-cycle for a complete blend, or three hours if the time for mixing after doping is taken into account. The time required to obtain a uniform mixture is obviously a function of the time taken to secure a complete circulation of the acid in the blender, as it was in the case of the preliminary mixers. There is the difference, however, that in the blenders there is no throttling of the circulation due to the presence of coils.

Time required for complete circulation of acid in the blender.

Considering the case of a blend of 9 feet of TNT mixed acid:—

Volume of acid in a blender 20 feet in diameter $= \frac{22}{7} \times (10)^2 \times 9$

$=$ approximately 2,830 cubic feet.

Diameter of propeller - - - - - - 18 inches.

Pitch of propeller - - - - - - - 24 „

Speed of stirrer - - - - - - - 145 r.p.m.

$\therefore$ Volume of acid raised per minute $= \frac{22}{7} \times (9)^2 \times 24 \times 145$ cubic inches $=$ approximately 886,000 cubic inches.

Allowing 10 per cent. for slip, viz. $=$ 88,600 cubic inches.

Actual volume lifted per minute $=$ 797,400 cubic inches.

$\therefore$ Time for complete circulation is $\frac{2,830 \times 1,728 \times 60}{797,400} = 368$ seconds, or approximately 6 minutes.

Doping. The method of calculating dopes was dealt with at considerable length in Section 2, and the present treatment of the subject is only concerned with the actual process involved. Successful doping obviously depends upon :—

(1) Reliable sampling.
(2) Reliable analysis.
(3) Careful measurement of the dips of the original blend and of the dope.
(4) Correct estimation of the strengths of the acids used.

There is one further source of error. Dopes are usually measured in a preliminary mixer, and, even assuming that the dope itself has been properly made, it is not a foregone conclusion that the dope will always reach the blender in the same form or amount as made in the mixer. In the first place, there is always a chance of the outlet valves of other mixers allowing acid to pass from them into the common main to blenders during the time in which the dope is being pumped to a blender from the mixer in which it is made. To guard against this, it is necessary to test these valves regularly and systematically. The practice is to test them every time a mix is made by noting any variation in the level of the acid in each mixer during every period when the bulk of acid remains stationary. This occurs when the sulphuric charge of 34½ inches is awaiting the addition of nitric acid; and again, whenever the addition of nitric or other acid is stopped to allow the mix to cool down. The same observation of level serves to test the soundness of coils and inlet valves, faults in either of which would cause a rise in level. The other error is due to the residual acid in the pipe-line between mixer and blender, which is seldom of the same composition as the dope. The maximum error due to this cause is here calculated for the case of the mixer situated farthest from the blending tanks.

Between this mixer and the blenders there is a length of 18 feet o 3-inch pipe and 154 feet of 4-inch pipe. Reckoning acid of gravit 1·830, these pipes contain 0·73 ton of acid. The usual dope being one of sulphuric acid, the principal resultant error when the pipe is full o mixed acid will be in the HNO_3 content of the blend.

The maximum HNO_3 content of mixed acid in the line is abou 32 per cent., and the HNO_3 contained in 0·73 ton of mixed aci containing 32 per cent. of HNO_3 will be 0·24 ton.

Taking the average final tonnage of a blend as 160 tons, the HNO of this blend, instead of being correct, would be too high by $\frac{0{\cdot}24 \times 100}{160}$ *i.e.*, 0·15 per cent.

This is well within the specification limits allowed for the mixe acid.

Development of heat.— Heat will be developed in the blending tan whenever doping is carried out. It is well to be quite clear as to th extent of this heating, and it can be realised most clearly by expressin it as a resultant rise in temperature.

The following figures were obtained experimentally by mixin 750 c.c. of TNT mixed acid with quantities of oleum, 98·6 per cen sulphuric acid, and 90 per cent. sulphuric acid, equivalent to 10-to dopes to a blend of 150 tons:—

Dope.	Rise in temperatur °C.
10 tons of oleum - - - - - -	5·7
10 tons of 98·6 per cent sulphuric acid - - -	1·0
10 tons of 90 per cent. sulphuric acid - - -	0·1

Since a sulphuric dope is usually measured in a mixer and the added to the blend, the rises of temperature indicated actually tal place in the mixed acid in the blender. The undesirability of treatin oleum dopes in this way is clear, and, as a general rule, they are avoide by aiming at an initial dilution slightly on the low side. If on an account a large oleum dope of 20 tons or so is required, the hea developed must be removed. This can be effected by pumping portion of the blend back to the preliminary mixers and adding the dope ther the mixture being cooled down before being pumped back to th blender. It is a safe policy never to pump or run direct to a blender any acid containing free SO_3.

A similar experiment was conducted in the case of MNT mixed acid, but in this case the amounts were calculated for a blend of 120 tons.

Dope.	Rise in temperature. °C.
10 tons of oleum - - - - - - - -	10·2
10 tons of 98·6 per cent. sulphuric acid - -	3·7
10 tons of 90 per cent. sulphuric acid - - -	1·2

It is still more necessary, therefore, in the case of this variety of mixed acid, to add an oleum dope to portions of the blend returned to the mixers

Loss of heat through radiation.

Up to the present, it has not been possible to get satisfactory determinations of this quantity by direct measurement, partly on account of the difficulty of measuring the temperature of the acid in the blenders with sufficient accuracy. A rough measure of this loss may be obtained, however, by assuming the radiation loss per square foot of blender surface to be of the same order as that obtaining for a mixer.

For mixed acid at a temperature of 42° C., the atmospheric temperature being 2° C.:—

Loss of heat per square foot of surface per hour = 68·9 C.H.U.

For mixed acid at a temperature of 30° C., the atmospheric temperature being 12° C.:—

Loss of heat per hour per square foot will be approximately—

$$\frac{68\cdot9 \times (30 - 12)}{(42 - 2)} = 31 \text{ C.H.U.}$$

Assuming that the radiating surface of the blender is 1,350 square feet, the loss of heat by radiation per hour will be approximately 42,000 C.H.U.

Taking the weight of a blend of TNT mixed acid as 150 tons, and its specific heat as 0·36, then—

Heat lost by this acid falling 1° C.

$$= 150 \times 2{,}240 \times 0\cdot36 = 120{,}960 \text{ C.H.U.}$$

∴ Fall in temperature per hour due to this radiation loss

$$= \frac{42{,}000}{120{,}960} = 0\cdot35^\circ \text{ C.}$$

This is under average conditions and gives some idea of the possible cooling which the mixed acid may undergo during its transit from the blending tanks to the nitrating houses, a period of about three days.

Physical behaviour of mixed Acids at low temperatures.—Some experiments were carried out at H.M. Factory, Oldbury, in order to determine the physical behaviour of various mixed acids when the temperature is lowered to about -30° C. The results showed that acids containing less than 70 per cent. of H_2SO_4 and 10 per cent. of HNO_3 can be cooled down to -30° C. without solidification taking place, whereas acids

containing 75 per cent. of H_2SO_4 and from 1 to 10 per cent. of HNO_3 gradually thicken and become solid as the concentration of the HNO_3 is increased or the temperature lowered.

STORAGE FOR FRESH MIXED ACIDS.

General Arrangement of Storage Tanks, &c.—Fig. 22 shows the general arrangement of the storage tanks for TNT and MNT mixed acids at Queen's Ferry. The tanks are erected on brickwork supports, with a fall of 2 inches away from the discharge end of the tanks so that sludge may be drawn off when necessary. The brickwork supports are constructed of good hard burned bricks laid in cement, the upper courses in contact with the tanks being acid-proof. From the brickwork forming the supports of one of the banks of tanks wing walls are built out to support the floor carrying the pumps. The ground between the brickwork and for a distance of about 10 feet all round it is covered with acid-proof bricks laid in tar and fireclay, the surface being sloped to permit of drainage. The level of this floor is made to be at least 9 inches above the surrounding ground level.

The tanks are erected in two banks of six tanks, each with a space between the ends of the tanks of about 6 feet, the low or sludge outlet ends being brought together, thus permitting all sludge to be taken away from a single alley-way. A platform is erected upon the walls above this alley-way giving access to the overflow pipes and sludge plug-valve gear, access to this platform being gained by a gangway over two of the tanks. At the discharge end of the bank of tanks remote from the pumping plant a platform is erected which gives access to the discharge valves, and this platform is reached by means of a steel ladder from the ground level. Above this is erected a platform giving access to the inlet piping to this bank of tanks. The latter platform is lead-covered so as to form a tray to collect any drips which may fall from the feed valves and joints. At the pumping plant end a gangway is erected over the tanks which gives access to the feed mains as shown.

The pumping plant, which is housed in completely by a wooden-framed building, consists of a set of Douglas pumps, each direct coupled to an electric motor. Three 4 ft. 6 in. diameter by 19 ft. long blow-casks are installed in case of failure of the pumps.

The fresh TNT mixed acid is pumped from the 20 feet by 12 feet blending tanks into a 3-inch mild steel main which passes over the storage tanks holding TNT acid, and is discharged into either of the tanks as required, a cast iron gland cock controlling the supply to each. The discharge from each of the tanks is led into a common 3-inch steel main, each discharge being controlled by a plug valve in the tank itself and a 3-inch cast steel valve outside the tank. From this main 3-inch branches are taken to two 3-inch Douglas pumps, the discharges of which are coupled together and connected to the main pipe line to the nitration houses; valves are provided on both suction and deliveries so that one pump may be operative and the other a reserve. A connection from the branch supplying one of the pumps is taken down to one of the blow casks situated below the pump platform, and the blow-cask discharge is connected to the common discharge from the pumps. Thus, for supplying TNT mixed acid to the nitrators there is one pump working, one pump in reserve, and one blow-cask in reserve. The arrangement of piping, pumps, and blow-casks for the fresh MNT mixed acid is exactly similar to that described above for TNT acid.

Details of Storage Tanks for mixed Acid.—Fig. 23 gives the details of the cylindrical steel tanks used for storing the fresh mixed nitrating acids. Each tank consists of a steel boiler shell tank, 9 feet diameter by 30 feet long, built up of ⅝-inch plates with single riveted joints throughout. One end plate is flanged and riveted to the shell plate, whilst the other end plate is attached to a 3½-inch by 3½-inch by ½-inch angle which is riveted to the outside of the shell. Each tank is fitted with a ¾-inch gauge-glass, air vent pipe, &c.

DISTRIBUTION OF ACIDS.

Arrangement of Acid Pipe-lines. Six mild steel pipes are led from the mixing plant, four 2-inch and one 3-inch pipe to the MNT section, and one 4-inch pipe to the TNT section. These pipes are supported on wooden trestles graded in height so that they have a uniform fall of approximately 1 in 750 from the steel mixers. These pipe-lines are provided with flanged joints spaced about 300 feet apart, the intermediate joints being made with ordinary screwed sockets; expansion bends are introduced at distances of approximately 600 feet.

The 2-inch lead spent acid pipes from the MNT and TNT plants are carried on the same trestles which carry the fresh acid pipes, and are laid so that they have a uniform fall of 1 in 750 to the spent acid tanks adjacent to the denitration plant.

Details of Trestles for Acid Pipe-lines.—The trestles are of timber, and consist of 4-inch by 4-inch posts toe-nailed to a 6-inch by 4-inch sill resting on a dry brick foundation as shown in Fig. 24. The caps are 6 inches by 4 inches, and the bracings to the main posts are 4 inches by 2 inches, and are spiked on. The trestles are spaced 15 feet centre to centre, and 6-inch by 3-inch joists are laid longitudinally across the caps, to which is nailed 2-inch open boarding upon which the pipe-lines are laid. Immediately below the cap of each trestle two 6-inch by 3-inch timbers are nailed to the posts. These project on one side 2 feet 4 inches beyond the cap, and have a 4-inch by 4-inch strut toed into the post to stiffen the outer end of the 6-inch by 3-inch timbers. On this cantilever projection a 2-inch decking is carried on 6-inch by 3-inch longitudinal joists, forming a walking platform for the examination of the pipes, the outer side of which is fitted with a wooden handrail. When the trestles have to carry in addition the spent acid, MNT, and toluene pipes, extensions to the trestles are made as shown in Fig. 24.

The trestles are graded from one end of the site to the other, in accordance with the particulars contained in the preceding paragraph.

To Face page 85.

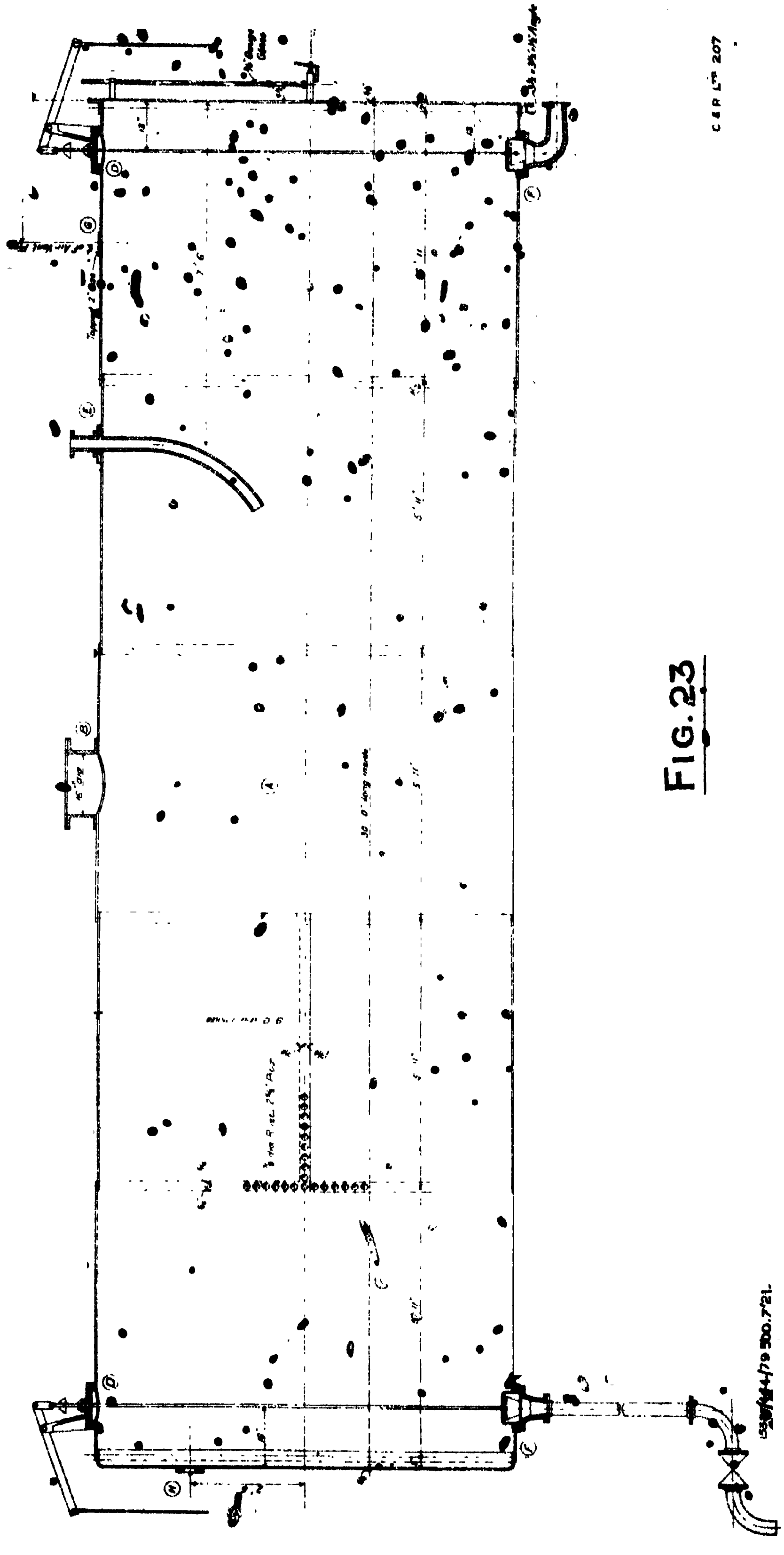


FIG. 23

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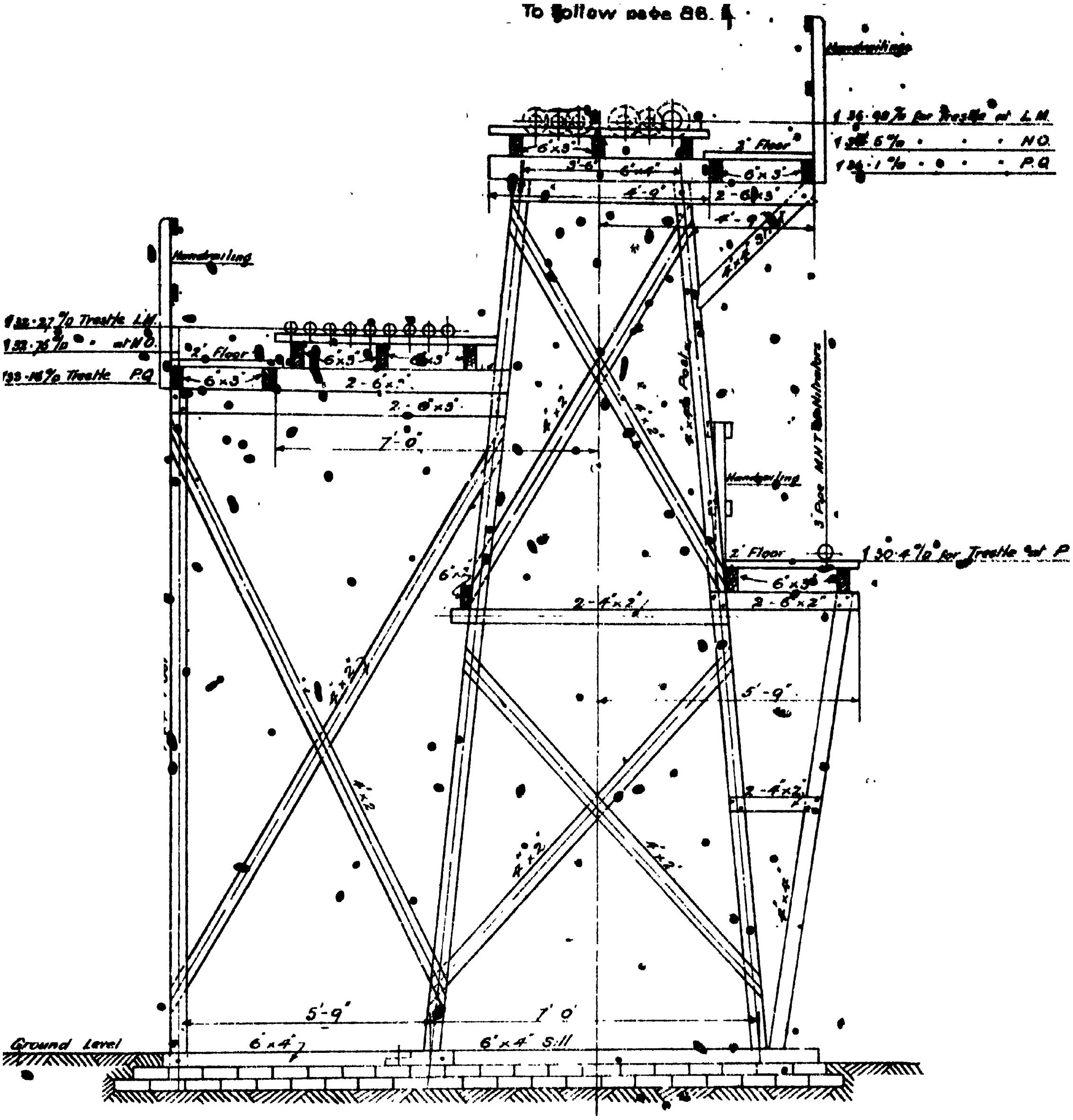
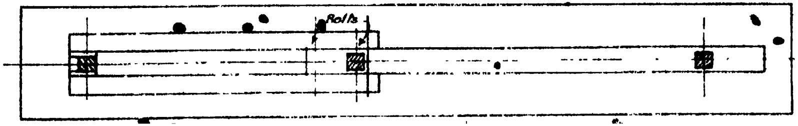
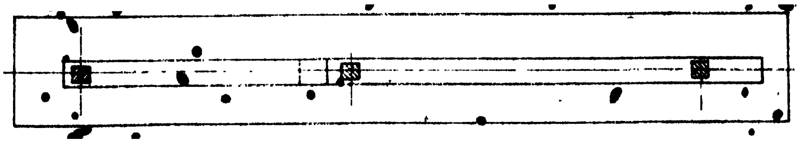


ELEVATION OF TRESTLE.



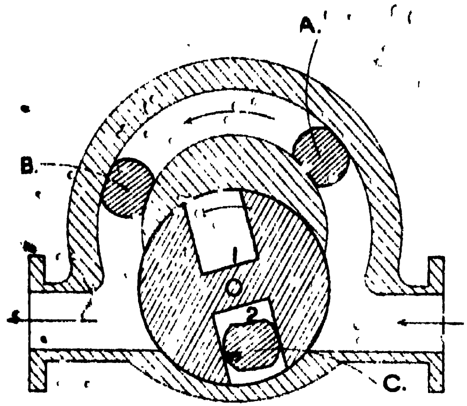
PLAN OF SILL.



ALTERNATE METHOD OF LENGTHENING SILLS.

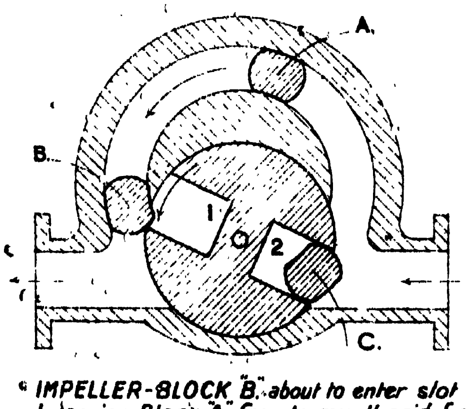
DIAGRAM SHOWING SUCCESSIVE POSITIONS OF THE PARTS OF A DOUGLAS PUMP DURING ONE THIRD OF A REVOLUTION.

Moving parts close shaded.
Fixed parts open shaded.



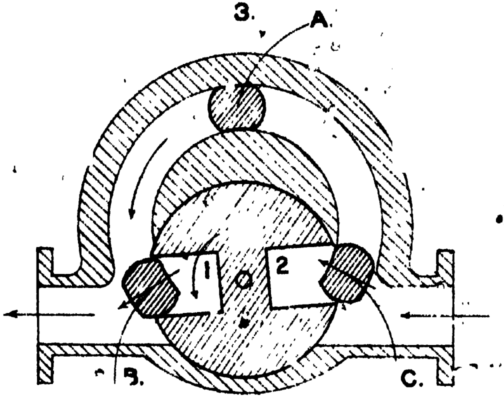
IMPELLER-BLOCK "C" returning to suction side of Pump.

2.



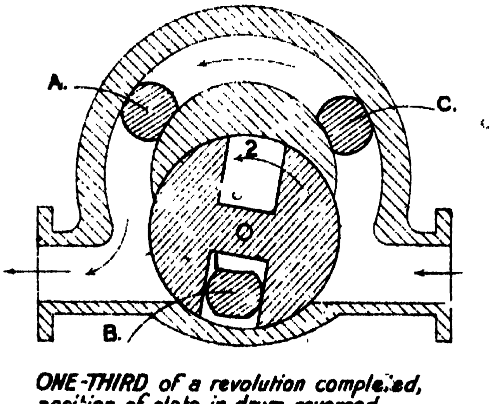
IMPELLER-BLOCK "B" about to enter slot 1. leaving Block "A" free to expell acid from circulating channel to outlet.

3.



BLOCK "B" passing in and Acid passing out of Slot 1.
BLOCK "C" passing out and Acid passing into Slot 2.
The acid passes mainly through holes in the Blocks.

4.



ONE-THIRD of a revolution completed, position of slots in drum reversed.

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Acid Pumps.—The type of pump originally installed at the mixing plant was the Douglas, and these pumps have been almost universally used at Queen's Ferry where the pumping of strong mixed acids is concerned.

The working of the Douglas pump is made quite clear by the accompanying diagram, Fig. 25. This shows that there are two circulations of acid in the pump :—

(*a*) The main circulation through the circular channel between the outer rim of the pump body and the semi-circular surface of the crescent-shaped block attached to the pump cover. This channel is rectangular in section and the acid passing through it is impelled by the blocks attached to the impeller, which exactly fit the cross-section of the channel.

(*b*) The minor circulation of acid in the "drum" of the pump. This acts primarily as a valve to shut off the inlet and outlet of the pump from each other, and at the same time it provides a means of securing the return of the impeller blocks from the outlet to the suction side of the pump.

For each revolution of the impeller the drum makes a revolution and a half. During each semi-rotation of the drum the slot in the upper position carries acid across from the suction to outlet side, where one of the impeller blocks enters the slot and expels its own volume of acid therefrom.

The acid is expelled from the slot of the drum just at the moment when the flow of acid through the pump outlet would otherwise be broken. The result is that the Douglas pump gives a continuous flow of acid, and, although the stream is not quite steady, it never stops altogether.

Efficiency of working.—The circulation channel only extends for two-thirds of the total circumference of the pump. Assuming it to be extended throughout the whole circumference, it is evident that the total amount of acid pumped during each revolution of the impeller (provided that no leakage back occurs) is equal to the volume of this complete circulation channel.

The acid carried round by the slots in the drum just compensates for the space taken up in the circulation channel by the three impeller blocks.

3-inch Pump.

Assuming a perfect fit in all parts, the amount of acid shifted by a 3-inch Douglas pump can be arrived at as follows :—

Outer diameter of circulation channel - - - = 14¾ inches.
Inner diameter of circulation channel - - - = 9¾ „
Mean diameter of circulation channel - - - = 12¼ „

Width of circulation channel - = 2½ inches.
Depth of pump (front to back) = 4 „
Speed of impeller - - = 75 r.p.m.
Volume of circulation channel = 3·1416 × 12¼ × 4 × 2½ cubic inches.
= 384·8 cubic inches.
Total volume pumped per hour = 384·8 × 75 × 60 cubic inches
= 1,731,600 cubic inches.
= 1,002 cubic feet.
Corresponding weight of water = 27·9 tons per hour.

Actual measurements have shown that the maximum tonnage which a 3-inch Douglas pump shifts is 47 tons of mixed acid of specific gravity 1·835. This quantity corresponds to 25·6 tons of water, so that the initial efficiency of the pump is about 91 per cent. of its calculated value.

2-inch Pump.

Outer diameter of circulation channel - - 9¾ inches.
Inner „ „ „ - - 5¾ „
Mean „ „ „ - - 7¾ „
Width „ „ - - 2 „
Depth of pump - - - - - - 3 „
Speed of impeller - - - - - 100 r.p.m.
Volume of circulation channel = 3·1416 × 7¾ × 3 × 2 cubic inches.
= 146·0 cubic inch.
Total volume pumped per hour = 146·0 × 100 × 60 cubic in.
= 876,000 cubic inches.
= 507 cubic feet.
Corresponding weight of water = 14·2 tons.

Actual measurements have shown that the maximum amount of acid shifted by a new 2-inch Douglas pump is about 21 tons of acid of specific gravity 1·835, which corresponds to 11·4 tons of water. A new 2-inch pump has, therefore, an efficiency of slightly more than 80 per cent.

The makers' specifications for these pumps are :—

(*a*) For the 3-inch pump 5,000 gallons per hour, which is equivalent to 22·3 tons of water per hour.

For the 2-inch pump 2,100 gallons per hour, which is equivalent to 9·4 tons of water per hour.

Both types of pump, therefore, when new, considerably exceed their specified capacities.

These rates of pumping seem to be fairly well maintained during the first month of continuous working. As the efficiencies of the pumps decline to 25 and 12 tons per hour respectively, two pumps are used together; the delivery lines are of ample size to allow of this being done. In the following table are set out some interesting data in connection with the operation of Douglas pumps at the mixing plant:—

DATA FROM OPERATION OF DOUGLAS PUMPS.

Size of pump.	Duty of pump	Size of electric motor used to drive pump.	Length of pipe line in feet.	Diameter of pipe line in inches.	Static head in feet.	Average tonnage of acid pumped per hour.	Life of pumps in months.	Life of pump in tonnage of acid pumped.
3-inch	TNT mixed acid from mixers to blenders.	5	150	4	11	31·0	5½	17,500
"	MNT mixed acid from mixers to blenders.	5	150	4	11	32·0	19	15,800
	TNT mixed acid from blenders to storage.	5	200	4	27	32·5	6½	20,6[illegible]0
	MNT mixed acid from blenders to storage.	5	200	4	27	32·0	19	15,800
	TNT mixed acid from storage to nitration houses.	5	2,400	4	3	32·5	6	19,800
2-inch	MNT mixed acid from storage to MNT section.	—	3,000	3	—	16·0	19	15,800
"	93 per cent. sulphuric acid for retort feed from mixer to storage.	4	1,830	3	11	12·0	3	12,000
"	90 per cent. sulphuric acid from Gaillard concentrators to storage.	2½	540	3	29	10·0	2¾	5,500
"	90 per cent. sulphuric acid from storage to Grillo oleum plant.	2½	1,830	3	11	14·5	6	20,000

The conditions which are essential for good working efficiencies appear to be as follows:—

(*a*) Cool acid: 32° C. to be a maximum temperature.

(*b*) Constant use: to prevent tendency to seize.

(*c*) The supply and delivery pipes should be of sufficient size to reduce friction to a minimum and to avoid any throttling effect; *e.g.*, a 2-inch Douglas pump having a 2½-inch outle should be fitted with 3-inch supply and delivery pipes.

Friction in the suction pipe causes a loss of power and increase the tendency for leakage of air through joints and glands. Friction in the delivery pipe is a waste of energy, and a cause of leaking joints both in pipes and pump glands. All 3-inch pumps, therefore, are fitte with 4-inch deliveries and 2-inch pumps with never less than 3-inch deliveries. The life of the pumps on the plant for mixing retor sulphuric acid has been increased by at least 25 per cent. by replacing a 2-inch by a 3-inch delivery pipe.

Effective life of pumps.—This is judged by either (*a*) the reduction of the quantity pumped to a ridiculously low figure, or (*b*) the corrosion or cracking of some vital part of the pump, particularly the impeller or the case.

Much t [illegible] the pump [illegible] is thought that strengthening would be necessary. Since the acid has been cooled down to 32° C., however, no instance of cracking has occurred; and, further, during the month of December, 1917, no pump repairs of any sort were necessary in the mixing house.

There is a marked difference in the effective lives of similar pumps dealing with different acids, or with the same acids at different temperatures.

(*a*) *TNT mixed acid* ($79 \cdot 5$ H_2SO_4; $17 \cdot 8$ HNO_3; $2 \cdot 7$ H_2O), if pumped at a temperature above about 32° C., causes either the impeller or the shafting of the pump to seize very readily. This usually puts the pump out of action until it has been overhauled and skimmed.

Whilst a 3-inch Douglas pump was in use at H.M. Factory, Oldbury, it was noticed that the castings increased slightly in size, it being necessary to ease the working parts periodically. This continued for about 5 months, and then in one week the castings decreased so much that it was necessary to instal a new pump. The practice afterwards adopted was to machine off $\frac{3}{1000}$ inch from the working parts of the pump as delivered by the maker. It was found that the working parts then increased in size sufficiently for satisfactory working. The pumps seize very soon if this is not done. This precaution is only necessary in the case of pumps used in connection with TNT mixed acid.

(*b*) *MNT mixed acid* (62 H_2SO_4; 21 HNO_3; 17 H_2O) has given no trouble. The 2-inch pumps used for delivering acid from the mixing plant to the MNT Section have needed practically no overhauling whatever.

(*c*) 90 *per cent. sulphuric acid.*—Queen's Ferry experience indicated that the Douglas pumps in use were attacked most by this variety of acid. This again appears to be largely a question of temperature, as the life of the 2-inch pumps used to deliver 90 per cent. sulphuric acid at 45° C. from the concentration plant to storage is less than half that of those delivering the same acid at 29° C. from storage to the oleum plant.

Cost of pumping acids.—In the accompanying table will be found some details regarding the cost of pumping. The costs given are exclusive of the maintenance of the electric motors and process labour charges involved therein.

COST OF PUMPING ACID.

Duty of pump.	Average temperature of acid pumped.	Life of pump in months.	Life of pump in acid, tons pumped.	Cost per ton of acid pumped. Power.	Maintenance. Material.	Maintenance. Labour.	Total.
	° C.			*d.*	*d.*	*d.*	*d.*
TNT mixed acid from mixers to blenders.	25	5½	1[illegible],000	0·04	0·50	0·07	0·61
TNT mixed acid from blenders to storage tanks.	25	6½	20,000	0·06	0·43	0·07	0·56
TNT mixed acid from storage tanks to nitration houses.	25	6½	20,000	0·04	0·43	0·07	0·54
90 per cent. sulphuric acid from concentration plant to mixers.	48	2¾	5,500	0·13	1·16	0·16	1·45
93 per cent. sulphuric acid for retort feed from mixer to storage.	30	3	12,000	0·11	0·53	0·04	0·6[illegible]
90 per cent. sulphuric acid from storage to oleum plant.	30	6	20,000	0·07	0·32	0·04	0·43

In the preceding table power is reckoned at 1*d.* per unit. The maintenance costs, the material cost for which includes cost of new pumps and parts, represent fair averages for the year 1918. It is evident from the figures shown that maintenance charges constitute the heaviest item in the working costs, particularly the cost of material.

As the efficiency of a pump decreases with continuous working, it is customary, when this figure has declined to below 50 per cent. of the maximum, to operate two pumps at the same time rather than to replace the pumps immediately. This course is taken in view of the low power cost in relation to the cost of renewal of the pump.

The least satisfactory case is shown by the pumps used to deliver 90 per cent. sulphuric acid from the concentration plant to the storage tanks at the mixers. As mentioned elsewhere, the most troublesome factor undoubtedly is the high temperature of the acid, which is mainly responsible for the excessive wear and tear. This is seen from the fact that when the temperature is reduced to about 20° C., the cost of pumping the same variety of acid is reduced approximately 70 per cent. Centrifugal pumps have since been substituted to some extent for Douglas pumps for use with this variety of acid.

In conclusion, it may be stated that the duty for which the Douglas pump can be said undoubtedly to have justified its selection is that of pumping mixtures of nitric and sulphuric acids. Provided that the acid be kept cool, little trouble is experienced.

SLUDGE FORMATION.

The subject of the formation and subsequent utilisation of sludge is one which demands considerable attention in factories using large quantities of acids, and it is one which well repays the time and thought given it owing to the valuable nature of the materials involved. The following remarks may be of interest as summarising in a short account the nature of the problems as a whole.

Types of Sludge and their causes.

(1) *Sludge formed by solution of iron in sulphuric acid or in weak spent acid.*—This consists almost entirely of ferric sulphate which is precipitated on concentration of the acid or on cooling. Such sludge often contains some of the ingredients (such as asbestos) of putties and cements which have been in contact with the acid or acid vapours.

(2) *Sludge formed by solution of nitrocellulose in a mixed acid.*—This material has been suggested as being possibly of value if recovered, but investigations do not support this view.

(3) *Sludge formed by solution of lead in acid.*—Examination of lead tanks used for storing weak sulphuric acid of 78–79 per cent. strength at temperatures ranging from 60°–100° C. revealed the fact that the extent and character of the destructive action varied as follows:—

(*a*) The whole surface of the tank covered by acid had been equally affected, or

(*b*) The action had been confined to local areas, more or less in the form of holes. These holes appeared to be of two kinds, viz.:—

(1) A countersunk hole having irregular walls.

(2) A hole cut through as though pierced with a sharp borer.

Difficulties resulting from Sludge formation.

(*a*) Blockage of pipes, valves, tower packing, &c.

(*b*) Bad conductivity, which affects the even heating of vessels containing mixed acids.

(*c*) Fixation of iron, lead, &c., by the acid with subsequent loss of—

(1) Acid.

(2) Vessels containing the acid.

(*d*) Loss of acid when vessels have to be sludged out, there being a layer of acid in immediate contact with the sludge.

(*e*) A so-called empty tank sometimes contains sludge at the bottom, and as this is acidic, corrosive action is always proceeding, thereby weakening the tank. This generally remains undiscovered until the tank is put into commission again.

Utilisation of Ferric Sulphate Sludge.—The four alternatives which present themselves in connection with the utilisation of this sludge (which, after filtration contains about 40 per cent. of free H_2SO_4) are as follows:—

(1) Utilisation in substitution for equivalent quantities of sulphuric acid in the manufacture of nitric acid by the retort process. This can be effected by puddling the sludge and pumping it by means of a centrifugal pump into lead boxes situated above the retorts. If so utilised, filtration of the sludge (*vide infra*) is unnecessary.

(2) Using the above method only the free sulphuric content of the sludge is utilised, the ferric sulphate being lost in the nitre cake. An alternative is to treat the sludge with scrap iron in order to recover the ferric sulphate and excess of sulphuric acid in the form of ferrous sulphate. It follows that this scheme is only practicable in the absence of nitric acid, and it is not therefore applicable in the case of sludge produced by fresh or spent mixed acids. This method of dealing with iron sulphate sludge is the general practice in many acid works.

(3) Filtration of the sludge in order to recover the bulk of the free acid which it contains.

(4) Distillation of the sludge and introduction of the sulphur trioxide so obtained at a convenient point in the acid cycle.

Filtration of Sludge.—The third method given above was for a variety of reasons the most suitable one to adopt at Queen's Ferry, and a brief description of the process may be of interest. In almost every case acid tanks are provided with outlets or run-off pipes to permit of the easy removal of the sludge therefrom. When it is considered desirable to sludge out the tanks as much acid is run off as is possible, and the sludge is then stirred up and run on to the filter. The tank is then thoroughly cleaned with the smallest possible quantity of water, and the latter is also run to the filter. The acid is run off and removed by means of an air lift or other suitable mechanical means, and the cake of sludge is allowed to settle for several days, during which period a further quantity of acid drains away. The product after treatment in this manner contains approximately 18 per cent. of H_2SO_4, and one cubic foot of the wet material weighs about 112 lb. The filter used consisted of a rectangular pottery receiver as used for weak nitric acid. This was packed with chequer brickwork, ring packing and graded quartz. Lead filters have also been in use and were packed in a similar manner to that described above.

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